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XLI. *Precession of the Spinning Top.*

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[Plates V, VI, VII, VIII.]

SIGN and direction require careful consideration on a diagram of an actual case of top motion, and of the convention to be observed in the representation of a rotation by a vector, on the figure in Flatland.

In this representation the vector is assimilated to a screw, and taken in usual right-handed, for a rotation to give advance along the direction of the vector.

According as the top motion is mostly in the neighbourhood of the upright position and zenith of the top, or near the nadir and downward vertical, it is convenient to measure from the zenith or nadir the angle θ of inclination of the axle to the vertical, as in figs. A and B.

But in both cases the vector of the precession in azimuth, as well as OG, the vector of constant impulse about the vertical, is measured upward, as would be required in a Steady Motion.

Fig. 3, p. 182, Phil. Mag. July 1922, was not drawn with G above O, as it should have been on this plan, and so leads to some awkward change of sign; so too the references to a figure on p. 190 should be made to a figure A, with zenith θ.

On this right-handed screw system, the vector OC of the rotation of the Earth would be drawn from the centre to

* Communicated by the Author.

the North Pole : such a rotation is called *deasil* in agriculture and *widdershins* if opposite, expressions familiar once to the ploughman and his team, in directing them to turn round.

Right and Left of the Sun are ancient expressions of doubtful meaning in direction, as we find in Herodotus and Xenophon. In his description of the voyage of circumnavigation of Lybia, sent out by Neco to sail down the Red Sea and return to Egypt by the Pillars of Hercules, Herodotus (iv. 42) declares his disbelief of the account brought back of the Sun being seen on the right hand, and we are left in doubt as to whether he means to the North or South, or if the equator was crossed.

After the battle of Cunaxa the Greeks are said by Xenophon to have marched away having the Sun on the right hand, and that would be to the East if marching North.

Aristotle (*de Cœlo*) discusses a right and left hand of the Heavens, as of a living animal. In Esplandian, the enchanted island of California is placed to the Right of the Indies; and to day a Scot will give the direction "Turn to your East," meaning to the Right.

Turner has ignored the Right and Left hand of the sky in his picture where the Sun is shown setting in the East; so that Jonah's lament over Nineveh will hold today, of a city where they cannot discern between their right hand and the left.

Sitting in a room with the Sun on the right hand is awkward for writing, in throwing the shadow of the hand on the paper; much clearer to have the Sun on the left.

Fig. A and B are repeated here, drawn according to these conditions; and it will be noticed that a change from one to the other, from zenith to nadir θ, can be carried out in strict analogy by a mere change of θ into $\pi-\theta$, a change of $\cos\theta$ into $-\cos\theta$, z into $-z$, with a change of sign of $Q=\frac{d\theta}{dt}$, and of $\frac{dQ}{dt}$, leaving $\sin\theta$ unaltered.

In the discussion of Steady Motion, with constant precession μ, and its stability, as before in § 12, OA is drawn vertically upward on both figures to represent $\lambda=\frac{g}{\mu^2}$, the height of the conical pendulum AB to accompany the axle at its steady inclination to the vertical.

Then in our notation, with preponderance Ma, lb-ft, and transverse moment of inertia $A=MK^2$, lb-ft^2,

$$\mathrm{OP}=l=\frac{A}{Ma}=\frac{K^2}{a},\ \text{ft},$$

is the S.E.P.L. of the top swinging as a pendulum in a

plane ; or if the top hangs down vertical at rest, and then rotates as a conical pendulum of small displacement with angular velocity n, $g = ln^2$, $gMa = An^2$; and it was proved (p. 191) that

$$L = \frac{g}{m^2} = \frac{\mathrm{OP}^2}{\mathrm{AP}^2}\mathrm{OA}$$

is the S.E.P.L. to beat time with the slight nutation of the axle on its steady motion, corresponding to an apsidal angle

$$\mu\frac{\pi}{m} = \pi\frac{\mathrm{OP}}{\mathrm{AP}}.$$

Thus L is increased and the motion becomes more sluggish by making AP as small as possible, as in the upward vertical position ; and if OP and OL are equal or nearly so, L becomes infinite or very large, and the motion is on the verge of instability.

On the diagram of fig. A, B, the length $l = \mathrm{OP}$ fixes the scale of the other geometrical quantities, such as OA, a, K^2, $\frac{A, C}{M}$.

But in the representation of the dynamical quantities, in OGKC, a length k is taken as the standard of the scale, and then with OG, OC $= \mathfrak{d}, \mathfrak{d}'$,

$$\frac{\mathfrak{d}, \mathfrak{d}'}{k} = \frac{G, CR}{2An} = \frac{h, h'}{n},$$

where $2An$ is the rotational impulse acquired by the top in falling about a horizontal axis from rest at the zenith through the nadir position (p. 181).

In accordance with previous notation (p. 190) and on fig. A, B, drawn to geometrical scale,

$$\frac{\mathrm{CK}}{k} = \frac{A\sin\theta\frac{d\psi}{dt}}{2An}, \qquad \frac{\mathrm{ON}}{k} = \frac{A\frac{d\psi}{dt}}{2An}, \quad . \quad . \quad . \quad (1)$$

and with ϕ the hour angle,

$$R = \cos\theta\frac{d\psi}{dt} + \frac{d\phi}{dt},$$

$$\frac{A\frac{d\phi}{dt}}{2An} = \frac{CR - A\cos\theta\frac{d\psi}{dt}}{2An} = \frac{\mathrm{OC} - \mathrm{MC}}{k} = \frac{\mathrm{OM}}{k}, \quad . \quad (2)$$

provided we take $A = C$, when the top is called spherical, a restriction on ϕ without influence on ψ, but making a

complete analogy between the ϕ and ψ relations; and ignoring dimensions of scale we may take

$$A\frac{d\psi}{dt}=\mathrm{ON},\qquad A\frac{d\phi}{dt}=\mathrm{OM}.$$

Fig. A.

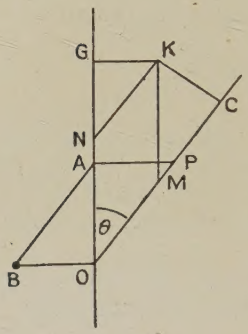


Fig. B.

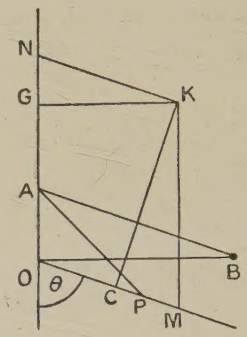


Fig. A.

$$\mathrm{GK}\sin\theta=\mathrm{OC}-\mathrm{OG}\cos\theta$$
$$\mathrm{CK}\sin\theta=\mathrm{OG}-\mathrm{OC}\cos\theta$$
$$\mathrm{OM}=\frac{\mathrm{OC}-\mathrm{OG}\cos\theta}{\sin^2\theta}$$
$$\mathrm{ON}=\frac{\mathrm{OG}-\mathrm{OC}\cos\theta}{\sin^2\theta}$$
$$A\frac{d\psi}{dt}=\frac{G-CR\cos\theta}{\sin^2\theta}$$
$$\frac{d\psi}{dt}=2\frac{h-h'z}{1-z^2}$$
$$=\frac{h+h'}{1+z}+\frac{h-h'}{1-z}$$
$$A\frac{d\phi}{dt}=\frac{CR-G\cos\theta}{\sin^2\theta}$$
$$\frac{d\phi}{dt}=2\frac{h'-hz}{1-z^2}$$
$$=\frac{h+h'}{1+z}-\frac{h-h'}{1-z}$$
$$\frac{d\varpi}{dt}=\frac{h'-hz}{E-z}$$

Fig. B.

$$\mathrm{GK}\sin\theta=\mathrm{OC}+\mathrm{OG}\cos\theta$$
$$\mathrm{CK}\sin\theta=\mathrm{OG}+\mathrm{OC}\cos\theta$$
$$\mathrm{OM}=\frac{\mathrm{OC}+\mathrm{OG}\cos\theta}{\sin^2\theta}$$
$$\mathrm{ON}=\frac{\mathrm{OG}+\mathrm{OC}\cos\theta}{\sin^2\theta}$$
$$A\frac{d\psi}{dt}=\frac{G+CR\cos\theta}{\sin^2\theta}$$
$$\frac{d\psi}{dt}=2\frac{h+h'z}{1-z^2}$$
$$=\frac{h+h'}{1-z}+\frac{h-h'}{1+z}$$
$$A\frac{d\phi}{dt}=\frac{CR+G\cos\theta}{\sin^2\theta}$$
$$\frac{d\phi}{dt}=2\frac{h'+hz}{1-z^2}$$
$$=\frac{h+h'}{1-z}-\frac{h-h'}{1+z}$$
$$\frac{d\varpi}{dt}=\frac{h'+hz}{E+z}$$

in our subsequent notation of $\cos\theta=z$, ϖ, and E.

With OH representing to scale the vector of the resultant impulse, and KH the component perpendicular to the plane

OGC of the paper, the dynamical equivalent of KH is $A\frac{d\theta}{dt}$, and on our right-handed system, HK is drawn away from the eye in fig. A, but towards us in fig. B.

It will save trouble in the statements if we ignore the distinction between a dynamical quantity and its geometrical representation, and treat them as equivalent in the equations; thus equating the velocity of H along KH to the impressed couple $An^2 \sin\theta$, and taking the radial component along GH,

$$\frac{d\mathrm{GH}}{dt} = An^2 \sin\theta \cos \mathrm{GHK} = An^2 \sin\theta \frac{\mathrm{HK}}{\mathrm{GH}}, \quad . \quad (3)$$

$$\mathrm{GH}\frac{d\mathrm{GH}}{dt} = A^2n^2 \sin\theta \frac{d\theta}{dt}, \quad . \quad . \quad . \quad . \quad (4)$$

and integrating

$$\mathrm{GH}^2 = 2A^2n^2(\mathrm{E} - \cos\theta), \quad \mathrm{OH}^2 = 2A^2n^2(\mathrm{F} - \cos\theta),$$
$$\mathrm{CH}^2 = 2A^2n^2(\mathrm{H} - \cos\theta), \quad . \quad . \quad . \quad (5)$$

or to a geometrical scale again

$$\mathrm{GH}^2 = \tfrac{1}{2}k^2(E - z), \quad \mathrm{OH}^2 = \tfrac{1}{2}k^2(F - z),$$
$$\mathrm{CH}^2 = \tfrac{1}{2}k^2(H - z), \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

where E, F, H are dynamical constants, connected by

$$F = E + 2\frac{h^2}{n^2} = H + 2\frac{h'^2}{n^2}, \quad \text{or} \quad F = E + 2\frac{\partial^2}{k^2} = H + 2\frac{\partial'^2}{k^2}, \quad . \quad (7)$$

Again, resolving the velocity of H at right angles to GH, with (ρ, ϖ) the polar coordinates of H in the horizontal plane GHK,

$$\rho\frac{d\varpi}{dt} = An^2 \sin\theta \sin \mathrm{GHK}$$
$$= An^2 \sin\theta \frac{\mathrm{GK}}{\mathrm{GH}} = An^2 \frac{\mathrm{OC} - \mathrm{OG}\cos\theta}{\mathrm{GH}}, \quad . \quad . \quad (8)$$

$$\rho^2\frac{d\varpi}{dt} = \tfrac{1}{2}kn(\partial' - \partial z), \quad \text{with} \quad \rho^2 = \tfrac{1}{2}k^2(\mathrm{E} - z), \quad . \quad (9)$$

with $\cos\theta = z$, equivalent to

Fig. A.	Fig. B.
$\frac{d\varpi}{dt} = \frac{h' - hz}{\mathrm{E} - z}$	$\frac{d\varpi}{dt} = \frac{h' + hz}{\mathrm{E} + z}$ . . (10)

The geometrical relation $GH^2=HK^2+KG^2$, replaced in dynamical units, becomes

$$2A^2n^2(E-\cos\theta)=A\left(\frac{d\theta}{dt}\right)^2+\left(\frac{CR-G\cos\theta}{\sin\theta}\right)^2, \quad (11)$$

$$\left(\frac{dz}{dt}\right)^2=2n^2(E-z)(1-z^2)-4(h'-hz)^2$$
$$=2n^2(F-z)(1-z^2)-4(h'^2-2hh'z+h^2)$$
$$=2n^2(H-z)(1-z^2)-4(h-h'z)^2=2n^2\mathrm{Z}, \quad (12)$$

$$\mathrm{Z}=z_1-z\,.\,z_2-z\,.\,z-z_3,$$

$$\infty>z_1>1,\ E,\ F,\ H>z_2>z>z_3>-1>-\infty, \quad (13)$$

in the sequence, leading to the Elliptic Function solution

$$z=z_2\,\mathrm{sn}^2\tfrac{1}{2}mt+z_3\,\mathrm{cn}^2\tfrac{1}{2}mt, \quad m^2=2n^2(z_1-z_3).$$

This is to zenith θ ; to the nadir θ, the sign of z must be altered, leaving the form of the equation unchanged.

But the further integration for ϖ, ψ, and ϕ introduces the Third Elliptic Integral, III. E. I.

This dynamical equation (11) may be interpreted as a combination of the Energy Principle with the constancy of component impulse G round the vertical and CR about the axle.

A vector treatment is given by W. C. Baker in the Physical Review, April 1922 ; W. F. Osgood, Bulletin American Math. Society, June–July 1921.

Fundamental Theorems of Dynamics can usually be presented in an incisive manner, shorter and more convincing than by reading into volumes of Victorian method, in analytical treatment by a procession of equations and approximation, and the use of Lagrange's method.

The dynamics of the top, spinning about a fixed point O, may be stated in two Propositions :—

A. The impulse vector OH describes a curve, in a horizontal plane in consequence of the constancy of the component impulse about the vertical ; and the projection of the C.G. of the top on this horizontal plane describes the hodograph of the curve of H, turned back through a right angle.

This is true universally of any unsymmetrical top.

But if the top has uniaxial symmetry :

B. The curve of H is a Poinsot herpolhode, and the angular velocity about the axle is constant.

Proposition A and B will give the "Top in two moves" ; and the motion is expressed by the elliptic function when the top has uniaxial symmetry.

But so far, for the general unsymmetrical top, the determination of the curve of H has defied Analysis.

In the general unsteady motion of the symmetrical top, the velocity of H imparted by the gravity couple $An^2 \sin\theta$ is along KH, and is equal to the rate of growth of $KH = A\frac{d\theta}{dt}$, together with the velocity of K carried round the vertical OG with angular velocity $\frac{d\psi}{dt}$; and with $\frac{d\theta}{dt} = Q$,

Fig. A.

$$An^2 \sin\theta = A\frac{dQ}{dt} + GK\frac{d\psi}{dt}$$
$$= A\frac{dQ}{dt} + \frac{GK \,.\, KC}{A \sin\theta}$$

$$\frac{d\,GK}{d\theta} = \frac{KC}{\sin\theta}, \quad \frac{d\,KC}{d\theta} = \frac{GK}{\sin\theta}$$

Fig. B.

$$An^2 \sin\theta = -A\frac{dQ}{dt} + GK\frac{d\psi}{dt}$$
$$= -A\frac{dQ}{dt} + \frac{GK \,.\, KC}{A \sin\theta} \quad . \quad . \quad . \quad (14)$$

$$\frac{d\,GK}{d\theta} = -\frac{KC}{\sin\theta}, \quad \frac{d\,KC}{d\theta} = -\frac{GK}{\sin\theta} \quad . \quad . \quad . \quad (15)$$

obvious geometrically on the figure.

Differentiating with respect to θ, with $d\theta = Q\,dt$,

$$\frac{1}{Q}\frac{d^2Q}{dt^2} = n^2\cos\theta - \frac{GK^2 + KC^2 - GK \,.\, KC\cos\theta}{A^2\sin^2\theta}$$
$$= n^2\cos\theta - \frac{GC^2 - 3GK \,.\, KC\cos\theta}{A^2\sin^2\theta}$$
$$= \left(n^2 + \frac{3OM \,.\, ON}{A^2}\right)\cos\theta - \frac{OK^2}{A^2},$$

$$\frac{1}{Q}\frac{d^2Q}{dt^2} = -n^2\cos\theta - \frac{GK^2 + KC^2 + GK \,.\, KC\cos\theta}{A^2\sin^2\theta}$$
$$= -n^2\cos\theta - \frac{GC^2 + 3GK \,.\, KC\cos\theta}{A^2\sin^2\theta}$$
$$= -\left(n^2 + \frac{3OM \,.\, ON}{A^2}\right)\cos\theta - \frac{OK^2}{A^2} \quad . \quad . \quad . \quad (16)$$

exact equations.

In a state of Steady Motion in regular precession μ, Q and $\frac{dQ}{dt}$ are zero; H and K coincide, and the velocity of K is

$$An^2 \sin\theta = \mu \,.\, GK, \quad An^2 = \mu \,.\, OM,$$
$$A^2n^2 = A\mu \,.\, OM = ON \,.\, OM, \quad \frac{ON}{OM} = \frac{A^2n^2}{A^2\mu^2} = \frac{n^2}{\mu^2} = \frac{\lambda}{l},$$

with

$$l = \frac{g}{n^2} = OP, \quad \lambda = \frac{g}{\mu^2} = OA; \quad \text{and} \quad OM \,.\, ON = \tfrac{1}{4}k^2,$$

to scale.

$$OK^2=OM^2+2OM\,.\,ON\cos\theta+ON^2 \qquad OK^2=OM^2-2OM\,.\,ON\cos\theta+ON^2$$

. . . (17)

$$\frac{OK^2}{A^2n^2}=\frac{OM}{ON}+2\cos\theta+\frac{ON}{OM} \qquad \frac{OK^2}{A^2n^2}=\frac{OM}{ON}-2\cos\theta+\frac{ON}{OM}$$

$$=\frac{n^2}{\mu^2}+2\cos\theta+\frac{\mu^2}{n^2} \qquad =\frac{n^2}{\mu^2}-2\cos\theta+\frac{\mu^2}{n^2}$$

. . . (18)

and in this Steady Motion, $\frac{1}{Q}\frac{d^2Q}{dt^2}=-m^2$, where

$$\frac{m^2}{n^2}=\frac{OK^2}{A^2n^2}-4\cos\theta=\frac{n^2}{\mu^2}-2\cos\theta+\frac{\mu^2}{n^2} \qquad \frac{m^2}{n^2}=\frac{OK^2}{A^2n^2}+4\cos\theta=\frac{n^2}{\mu^2}+2\cos\theta+\frac{\mu^2}{n^2}$$

$$=\frac{\lambda}{l}-2\cos\theta+\frac{l}{\lambda}=\frac{AP^2}{OA\,.\,OP} \qquad =\frac{\lambda}{l}+2\cos\theta+\frac{l}{\lambda}=\frac{AP^2}{OA\,.\,OP},$$

. . . (19)

a result obtained, without approximation, showing that the slightest tremor will appear in a small nutational velocity $Q=Q_0\cos(mt+\epsilon)$, beating $m/2\pi$ times a second, with an apsidal angle, from node to node, as stated above,

$$\Psi=\mu\frac{\pi}{m}=\pi\frac{OP}{AP}.$$

With $G=CR>2An$, the top can spin steadily upright in the zenith position ; then in general steady motion

$$OC=OM+MC, \quad \text{or} \quad CR=\frac{An^2}{\mu}+A\mu\cos\theta, \quad \text{with} \quad \cos\theta=1,$$

. . . (20)

is a quadratic for μ, the two independent circlings of the axle round the vertical, adding up to the general epicycle motion, seen in the top when spinning upright, asleep.

To lay off OA, OA′ in fig. A, to represent the two lengths of $\lambda=g/\mu^2$, GO is produced down to P, making $OP=l=g/n^2$,

$$\frac{CR}{An}=\frac{n}{\mu}+\frac{\mu}{n}\cos\theta, \text{ or } 2\frac{OC}{k}=\frac{OS}{OP}+\frac{OP}{OS}\cos\theta,$$

with OS the G.M. of OA, OP on the horizontal through O, and ASP a right angle.

To solve this quadratic for OS geometrically, draw the horizontal line NR at a depth $ON=OP\cos\theta$ below O, crossing the circle on OP in R ; then RP produced will meet the vertical line DE at a distance $OD=(\partial'/k)OP$ from O in E, centre of a circle of radius RE, crossing the horizontal through O in S, S′, with $OS+OS'=OD$,

$$OS\,.\,OS'=OR^2=OR^2=OP\,.\,ON=OP^2\cos\theta.$$

Then SA, S′A′ at right angles to PS, PS′ will cut off the length OA, OA′.

So, too, for a prolate solid, like a china egg, spun upright on a table, discussed in R.G.T. p. 273, we take in the notation there

$$l=\frac{g}{n^2}=\frac{\frac{A}{M}+z^2}{z-\rho}, \quad k=2(z-\rho), \quad \frac{\partial}{k}=\frac{\frac{C}{M}+z\rho}{\frac{A}{M}+z^2}\cdot\frac{R}{2n},$$

in the equations of the top, with $\partial=k$ on the verge of stability, and then the energy is

$$\frac{CR^2}{2g}=\frac{2C\,.\,\frac{A}{M}+z^2\,.\,z-\rho}{\left(\frac{C}{M}+z\rho\right)^2}, \quad \text{or} \quad \frac{2A(z-\rho)}{\frac{C}{M}}\text{ ft. lb,}$$

on a smooth table.

Spinning upright inside a cup-shaped cavity, of radius of curvature ρ', replace $\frac{1}{\rho}$ by $\frac{1}{\rho}-\frac{1}{\rho'}$; and change the sign of ρ' if the body is spinning on a rounded summit.

But with $G=CR<2An$, the upright position is unstable; the axle will leave the zenith and ultimately reach an inclination θ_3, where

$$\cos\tfrac{1}{2}\theta_3=\frac{h}{n}=\frac{CR}{2An}.$$

Then reckoning the time from this lower position,

$$\sin\tfrac{1}{2}\theta=\sin\tfrac{1}{2}\theta_3\,\operatorname{sech}\tfrac{1}{2}mt, \quad m=2n\sin\tfrac{1}{2}\theta_3\,; \quad . \quad (21)$$

so that after another infinite time the axle will reach the upright zenith position again.

And for the azimuth ψ,

$$\psi-ht=\cos^{-1}\frac{\cos\frac{1}{2}\theta_3}{\cos\frac{1}{2}\theta}=\tan^{-1}(\tan\tfrac{1}{2}\theta_3\,\operatorname{th}\tfrac{1}{2}mt)$$

$$=\tfrac{1}{2}\cos^{-1}\frac{1+\cos\theta_3\operatorname{ch}mt}{\operatorname{ch}mt-\cos\theta_3}=\tfrac{1}{2}\sin^{-1}\frac{\sin\theta_3\operatorname{sh}mt}{\operatorname{ch}mt-\cos\theta_3}, \quad . \quad (22)$$

a relation connecting true anomaly $2(\psi-ht)$ with hyperbolic excentric anomaly mt in an hyperbolic orbit of excentricity $\sec\theta_3$; also

$$\cos\tfrac{1}{2}\theta\cos(\psi-ht)=\cos\tfrac{1}{2}\theta_3,$$

$$\cos\tfrac{1}{2}\theta\sin(\psi-ht)=\sin\tfrac{1}{2}\theta_3\operatorname{th}\tfrac{1}{2}mt. \quad . \quad . \quad . \quad (23)$$

In the herpolhode curve (ρ, ϖ) described by the impulse vector OH, $E=1$, $\frac{d\varpi}{dt}=h=h'$, $\rho^2=GH^2=\frac{1}{2}k^2(1-\cos\theta)$,

$$\rho=k\sin\tfrac{1}{2}\theta=k\sin\tfrac{1}{2}\theta_3\,\mathrm{sech}\,(\varpi\tan\tfrac{1}{2}\theta_3),$$
$$\rho\,\mathrm{ch}\,(\varpi\tan\tfrac{1}{2}\theta_3)=\partial\tan\tfrac{1}{2}\theta_3, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (24)$$

a curve circling round the origin G, and reaching it as an asymptotic point, a separating herpolhode.

If a tap is given while the top is spinning upright, the axle will pass periodically through the zenith ($z_2=1$), and describe a Rosette curve, so called by Klein ; the H curve will then be enclosed between two circles, and will have cusps on the outer circle, pointing to G.

A tap in the nadir position will create another similar Rosette figure, and the curve of H will then have cusps pointing away from G on an inner circle, and here $z_3=-1$.

But these herpolhode H curves are of general elliptic character.

Thus in an upper Rosette,

$$\sin\tfrac{1}{2}\theta=\sin\tfrac{1}{2}\theta_3\,\mathrm{cn}\,\tfrac{1}{2}mt, \quad h=h', \quad \kappa'=\sin\tfrac{1}{2}\theta_3/\mathrm{sh}\tfrac{1}{2}\theta_1,$$

and in a lower Rosette, to nadir θ,

$$\sin\tfrac{1}{2}\theta=\sin\tfrac{1}{2}\theta_3\mathrm{sn}\,\tfrac{1}{2}mt\ ; \quad h=-h', \kappa'=\cos\tfrac{1}{2}\theta_2/\mathrm{ch}\,\tfrac{1}{2}\theta_1\ ;$$

and in an Intermediate curve, where $z_1=1$, and to zenith θ,

$$\sin\tfrac{1}{2}\theta=\sin\tfrac{1}{2}\theta_3\,\mathrm{dn}\,\tfrac{1}{2}mt, \quad h=h', \quad \kappa'=\sin\tfrac{1}{2}\theta_2/\sin\tfrac{1}{2}\theta_3.$$

The axle will start from a cusp if $G=CR\cos\theta_2$, $h=h'z_2$, $H=z_2$, and will proceed to describe a curve to be identified as a gravity brachistochrone on the sphere.

In the special case given before on p. 183,

$$\theta_3=\tfrac{1}{2}\pi, \quad \cos\theta_2=\kappa, \quad \cos\theta=\cos\theta_2\,\mathrm{sn}^2\tfrac{1}{2}mt=\kappa\,\mathrm{sn}^2\tfrac{1}{2}mt,$$

$$\tan(\psi-ht)=\sqrt{\frac{\cos\theta\,.\cos\theta_2-\cos\theta}{1-\cos\theta_2\cos\theta}}$$
$$=\frac{\kappa\,\mathrm{sn}\,\tfrac{1}{2}mt\,\mathrm{cn}\,\tfrac{1}{2}mt}{\mathrm{dn}\,\tfrac{1}{2}mt}=\sqrt{\frac{1-\mathrm{dn}\,mt}{1+\mathrm{dn}\,mt}},$$

$$\cos 2(\psi-ht)=\mathrm{dn}\,mt, \quad \psi=ht+\tfrac{1}{2}\cos^{-1}(\mathrm{dn}\,mt)\ ; \quad . \quad . \quad (25)$$

$$\tan(\phi-h't)=\sqrt{\frac{\cos\theta\,.1-\cos\theta_2\cos\theta}{\cos\theta_2-\cos\theta}}$$
$$=\frac{\mathrm{sn}\,\tfrac{1}{2}mt\,\mathrm{dn}\,\tfrac{1}{2}mt}{\mathrm{cn}\,\tfrac{1}{2}mt}=\sqrt{\frac{1-\mathrm{cn}\,mt}{1+\mathrm{cn}\,mt}},$$

$$\cos 2(\phi-h't)=\mathrm{cn}\,mt, \quad \phi=h't+\tfrac{1}{2}\,\mathrm{am}\,mt. \quad . \quad . \quad . \quad . \quad (26)$$

In this case we can write the equations

$$(1+\cos\theta)\exp(\phi+\psi-qt)i=\surd(\sec\theta_2-\cos\theta\,.\,\cos\theta_2-\cos\theta)$$
$$+i(\surd\sec\theta_2+\surd\cos\theta_2)\surd\cos\theta=2\alpha^2e^{-qti},\quad .\quad (27)$$

$$(1-\cos\theta)\exp(\phi-\psi-q't)i=\surd(\sec\theta_2-\cos\theta\,.\,\cos\theta_2-\cos\theta)$$
$$+i(\surd\sec\theta_2-\surd\cos\theta_2)\surd\cos\theta=2\gamma^2e^{-q'ti},\quad .\quad (28)$$

$$q,\ q'=h\pm h'=n\surd(2\sec\theta_2)\pm n\surd(2\cos\theta_2),\quad .\quad (29)$$

and so identify a special algebraical case of Klein's parameters α, β, γ, δ of his Kreisel-Theorie, defined in terms of Euler's angles θ, ϕ, ψ by

$$\alpha=\cos\tfrac{1}{2}\theta\exp\tfrac{1}{2}(\phi+\psi)i,\qquad \beta=i\sin\tfrac{1}{2}\theta\exp\tfrac{1}{2}(-\phi+\psi)i,$$
$$\gamma=i\sin\tfrac{1}{2}\theta\exp\tfrac{1}{2}(\phi-\psi)i,\qquad \delta=\cos\tfrac{1}{2}\theta\exp\tfrac{1}{2}(-\phi+\psi)i,$$
$$\alpha\delta=\cos^2\tfrac{1}{2}\theta,\quad \beta\gamma=-\sin^2\tfrac{1}{2}\theta,\quad \alpha\delta-\beta\gamma=1.$$

Generally in any cusp motion, the hour angle ϕ is non-elliptic,

$$\sin\theta\cos(\phi-h't)=\surd(z_1+z_3\,.\,z_2-z),$$
$$\sin\theta\sin(\phi-h't)=\surd(z_1-z\,.\,z-z_3),\quad .\quad .\quad .\quad (30)$$

$$\tan(\phi-h't)=\sqrt{\frac{z_1-z\,.\,z-z_3}{z_1+z_3\,.\,z_2-z}}=\sqrt{\frac{z_1-z_3}{z_1+z_3}}\cdot\frac{\mathrm{dn}\,\frac{1}{2}mt\,\mathrm{sn}\,\frac{1}{2}mt}{\mathrm{cn}\,\frac{1}{2}mt}$$
$$=\sqrt{\frac{z_1-z_3}{z_1+z_3}}\sqrt{\frac{1-\mathrm{cn}\,mt}{1+\mathrm{cn}\,mt}}=\sqrt{\frac{z_1-z_3}{z_1+z_3}}\tan(\tfrac{1}{2}\,\mathrm{am}\,mt),\quad .\quad .\quad .\quad (31)$$

connecting true anomaly $2(\phi-h't)$ with excentric anomaly $\mathrm{am}\,mt$ in an elliptic orbit of excentricity z_3/z_1.

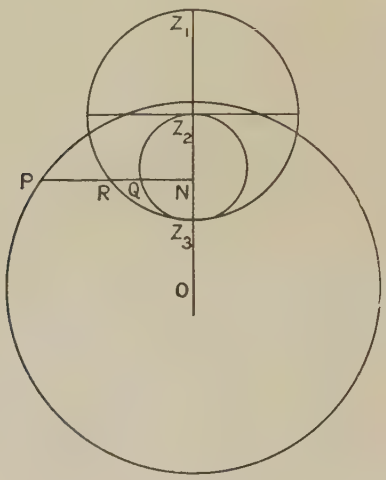
The brachistochrone cusp motion of the axle is rectifiable in the form

$$\cos\tfrac{1}{2}\frac{s}{l}=\mathrm{dn}\,\tfrac{1}{2}mt=\sqrt{\frac{z_1-z}{z_1-z_3}},\quad .\quad .\quad .\quad (32)$$

for s the length of the arc measured from the cusp described by the point P on the axle, $\mathrm{OP}=l$.

Marking the points Z_1, Z_2, Z_3 on the vertical at height lz_1, lz_2, lz_3 above O, draw the circle on diameter Z_1Z_3 and Z_2Z_3; then if PRQN is drawn horizontal, the arc s is $\frac{1}{2}l$ times the angle OZ_1R, in cusp motion.

Fig. 1.



And in the general top motion, the point P moves at the same level as R oscillating on the arc of the circle on Z_1Z_3 below Z_2, or as Q performing complete revolutions of the circle on Z_2Z_3, each moving in a field of gravity of appropriate strength G in plane pendulum motion,

$$\frac{G}{g}=\left(\frac{z_1-z_3}{z}\right)^2 \quad \text{or} \quad \left(\frac{z_2-z_3}{z}\right)^2.$$

Any special curve in top motion is worth putting on record, an oasis in the desert of General Theory.

Great variety of pattern is obtainable, in the simple pseudo-elliptic cases above of ψ and ϕ, by the variation of the secular term ht or $h't$ at disposal.

But these curves are not algebraical, and to obtain an algebraical result the secular term must be cancelled; variety of pattern is then obtained by choosing an aliquot part of a period as the parameter of the III.E.I.; this has been developed in the Report on Gyroscopic Theory (R.G.T.), and shown here in Plates V, VI, VII, drawn by Sir George Hadcock, calculations by Col. R. L. Hippisley.

Thus for a bisection of the period, the algebraical result for ψ is of the form, to the nadir vertical (Plate V.)

$$\sin^2\theta\cos 2\psi=(z+\tfrac{1}{2}.z_1+z_2)\surd(z-z_1.z-z_2),$$

$$\sin^2\theta\sin 2\psi=R\surd(2.z_3-z), \quad . \quad . \quad . \quad . \quad . \quad . \quad (33)$$

$$z_3=\frac{3-2\kappa+3\kappa^2}{(1+\kappa)\surd(9-14\kappa+9\kappa^2)}, \quad z_2, z_1=\frac{3-5\kappa, -5+3\kappa}{\surd(9-14\kappa+9\kappa^2)},$$

$$R=\frac{4(1-\kappa)\surd(1+\kappa)}{(9-14\kappa+9\kappa^2)^{\frac{3}{4}}}.$$

Introducing a Quadric Transformation, as in R.G.T. p. 121,

$$\kappa=\frac{1-\gamma'}{1+\gamma'}, \quad \surd\kappa\,\mathrm{sn}\,2eK=\gamma\,\mathrm{sn}\,eG\,\mathrm{sn}\,(1-e)G,$$

the result can be written

$$\tfrac{1}{2}M^2\sin\theta e^{\psi i}=\frac{\gamma'\,\mathrm{cn}\,eG}{\gamma\,\mathrm{dn}^2eG}+i\frac{\gamma'\,\mathrm{cn}\,(1-e)G}{\gamma\,\mathrm{dn}^2(1-e)G},$$

$$\tfrac{1}{2}M^2\gamma\theta'\sin\theta e^{\psi i}=\mathrm{cn}\,eG\,\mathrm{dn}^2(1-e)G+i\,\mathrm{cn}\,(1-e)G\,\mathrm{dn}\,eG,$$

$$\tfrac{1}{2}M^2\sin\theta_3=\frac{\gamma'}{\gamma}, \quad M^2=\frac{\surd(1+8\gamma'^2)}{\gamma^2},$$

$$\frac{\partial}{k}=\frac{\gamma'}{(1+8\gamma'^2)^{\frac{1}{4}}}, \quad \frac{\partial'}{k}=\frac{3\gamma'}{(1+8\gamma'^2)^{\frac{3}{4}}}; \quad . \quad . \quad (34)$$

and the herpolhode curve H of impulse is given in

$$M\frac{\rho}{k}e^{\varpi i}=\frac{\gamma'\rho}{\gamma\delta}=\mathrm{cn}\,eG+i\,\mathrm{cn}\,(1-e)G, \quad . \quad . \quad (35)$$

with the time $t=e\mathrm{T}$.

Set two pendulums swinging, to modulus γ, in perpendicular planes $x\mathrm{O}z$, $y\mathrm{O}z$, half a beat out of phase; with inclination a, b at time t,

$$\tan\tfrac{1}{2}a=\frac{\gamma}{\gamma'}\mathrm{cn}\,e\mathrm{G}, \quad \sin\tfrac{1}{2}a=\gamma\,\mathrm{sn}\,(1-e)\mathrm{G}, \quad \cos\tfrac{1}{2}a=\mathrm{dn}\,(1-e)\mathrm{G},$$

$$\frac{\rho}{\delta}e^{\varpi i}=\tan\tfrac{1}{2}a+i\tan\tfrac{1}{2}b, \quad \sin\theta e^{\psi i}=\frac{\sin a+i\sin b}{\surd(1+8\gamma'^2)}.$$

If GM, GN are the coordinates of H in the invariable plane through G,

$$\mathrm{OM}\,.\,\mathrm{ON}=\frac{\partial^2}{\gamma'},\quad \cos \mathrm{MON}=\gamma',$$

MON is the modular angle of γ, and the rolling polhode curve is a plane hyperbola.

There will be cusps when $\gamma'=\frac{1}{2}=\cos 60°$; and then

$$\kappa=\tfrac{1}{3},\quad \theta_3=30°,\quad \sec\theta_2=\surd 3=-z_1,\quad \frac{\partial,\partial'}{k}=\frac{1}{2\sqrt[4]{3}},\quad \frac{\sqrt[4]{3}}{2};$$

$$(\sin\theta e^{\psi i})^2=(\cos\theta+\sec\theta_2)^{1,2}(\cos\theta-\cos\theta_3)^{3\,2}$$
$$+i(\sec\theta_3)^{3/2}(\cos\theta_3-\cos\theta)^{1/2}.$$

A figure is given (Plate VIII, and included in Plate V) of an algebraical four-fold gyroscopic motion, drawn by Sir George Hadcock, for modulus $\kappa=\sin 75°$, $\gamma'=\cos 89°$, with the dotted interior curve of impulse, the herpolhode of H; the other dotted part is the curve of P in the lower hemisphere.

An attempt is made to show with it a Pseudo-regular Precession in a curve of 40 small loops, drawn for a modular angle 10° of κ; but the representation did not come out very distinct, as it is the projection of a looped curve on a steep part of the sphere; although seen sideways the loops are distinct and rounded and form a bold flourish scroll, thus

The curve was added also surrounding the figure as a necklace, a Regular Precession in 24 waves, going 7 times round, drawn for modular angle 1° of κ, as in a swift whirling of a spherical pendulum.

In a figure of a trisection of a period, an algebraical case of motion will be given by

$$(\sin\theta e^{\psi i})^3$$
$$=(Qz+R)\surd(z_1-z)+i(z^2+Az+B)\surd(z_2-z\,.\,z-z_3)$$

or

$$(Qz+R)\surd(z_2-z)+i(z_2+Az+B)\surd(z_1-z\,.\,z-z_3),\quad (36)$$

a curve in three or six loops (Plates VI, VII).

Thus with six cusps, and $z=\cos\theta$ to the nadir,

$$\kappa=\sin 15°,\quad \theta_2=60°,\quad \frac{\partial,\partial'}{k}=\tfrac{1}{2},\,1;$$

$$(\sin\theta e^{\psi i})^3=(2z-1)^{3/2}+i(1-z+z^2)\surd(2-2z-z^2);$$

and with three cusps we find

$$\frac{\kappa}{\kappa'} = 2 - \sqrt[3]{4} = \tan\theta_2 \sin\theta_3, \quad \sin\theta_3 = \sqrt[3]{4} - \sqrt[3]{2},$$

$$\tan\theta_2 = \sqrt[3]{2}, \quad z_1 = -\operatorname{ch}\theta_1, \quad \operatorname{sh}\theta_1 = \frac{1}{\sqrt[3]{2}};$$

$$\frac{\partial, \partial'}{k} = \frac{\sqrt{(\sqrt[3]{2}-1)}}{\sqrt[3]{4}} \left[\frac{1}{\sqrt[4]{(\sqrt[3]{4}+1)}}, \ \sqrt[4]{(\sqrt[3]{4}+1)} \right],$$

from which the equation can be constructed.

And so on, for higher aliquot parts, as discussed in R.G.T.

To exterminate an approximation, and to replace it by an exact treatment of greater simplicity and conviction, this should be the object of modern procedure in the rediscussion of a familiar problem in former Theory.

Thus in our discussion of Small Oscillation in (19) on a state of Steady Motion the equations were exact, and the word *approximate* was banished as not conducive to conversion in the mind of a young Berkeley, devoted to Rigour of Argument.

XLII. *On Tidal Stresses and Continental Displacements.* *By* H. H. Poole, *Sc.D.* *

IN view of the very great interest which is at present being displayed in the question of continental displacements, it seems to be worth while to draw attention to the fact that, at the present day, the tangential stresses due to tidal action, whether oceanic or crustal, would appear to be absolutely incapable of causing appreciable horizontal motion in large land-masses. This has already been commented on by Dr. H. Jeffreys at the British Association Meeting at Hull †; but the following simple demonstration may be of interest.

Taking the mass of the Earth as $5{\cdot}99 \times 10^{27}$ grams, and its equatorial radius as $6{\cdot}38 \times 10^{8}$ cm., we find that its moment of inertia (I) about its axis is $9{\cdot}74 \times 10^{44}$ gram sq. cm. Its angular velocity (ω) is about $7{\cdot}29 \times 10^{-5}$ radian per second.

Let us assume that in one century the day increases in length by 0·001 second. This figure has recently been

* Communicated by the Author.

† 'Nature,' Jan. 6, 1923, p. 31.

quoted by Prof. Eddington * as a probable measure of the retardation. It implies that each century is 36·5 seconds longer than the preceding one. The corresponding reduction in ω is given by the equation

$$-\frac{\delta\omega}{\omega} = \frac{0{\cdot}001}{86{,}400} = 1{\cdot}16 \times 10^{-8},$$

$$\therefore \quad -\delta\omega = 8{\cdot}45 \times 10^{-13};$$

since this occurs in 100 years

$$-\frac{d\omega}{dt} = \frac{8{\cdot}45 \times 10^{-13}}{100 \times 365 \times 86{,}400} = 2{\cdot}68 \times 10^{-22}.$$

Hence loss of moment of momentum $= -I\frac{d\omega}{dt} = 2{\cdot}6 \times 10^{23}$ dyne cm. Now assume, as a first approximation, that the tangential stresses causing this retardation are uniformly distributed over the entire surface area, $5{\cdot}1 \times 10^{18}$ sq. cm. The average distance of the crust from the axis being $5{\cdot}0 \times 10^{8}$ cm., the required stress would be

$$\frac{2{\cdot}6 \times 10^{23}}{5{\cdot}0 \times 10^{8} \times 5{\cdot}1 \times 10^{1}} = 1{\cdot}02 \times 10^{-4} \text{ dyne per sq. cm.},$$

i. e. only about one kilogram weight per square kilometre. This figure is so small that evidently, even if considerable concentration of the tangential forces on particular areas occurs, we should have to assume a rate of retardation quite incompatible with astronomical evidence, in order to account for the occurrence of stresses capable of causing appreciable relative movements involving distortion or fracture of the crust †.

It would seem then that, if tidal stresses have played a part in the history of the continents, they must have done so in past epochs, when, owing to crustal weakness or the closer proximity of the Moon, they were far more powerful than at present. This view accords well with the theory of continental displacement suggested by Dr. Joly in a forthcoming communication to the Royal Society.

Royal Dublin Society,
January 16, 1923.

* 'Nature,' Jan. 6, 1923, p. 20.

† So little is known of the sub-crustal conditions, that it appears to be conceivable that the minute stresses due to tidal action might cause a slow rotational motion of the crust as a whole relative to the interior, as has recently been suggested by Prof. Eddington. (Nature, *loc. cit.*)

XLIII. *On the Solution of the Representative Differential Equation of the Triode Oscillator.* *By* E. V. Appleton, *M.A., D.Sc., and* W. M. H. Greaves, *M.A., St. John's College, Cambridge**.

AMONG the modern methods of producing sustained electrical oscillations that involving the use of a thermionic tube is by far the most flexible and convenient. Thus with a triode or dynatron oscillation generator a range of frequencies from 1 to 10^8 per second is now available for all kinds of physical investigations. In everyday wireless practice continuous-wave triode generators are gradually replacing the spark generators of Hertz and Marconi, and thus the theoretical problems of radio-telegraphic reception are being simplified in that the old problems of damped vibrations are being replaced by the simpler ones of undamped vibrations. But the simplification ends with reception, for the evolution of the continuous-wave generator has given rise to a whole series of theoretical problems which have not hitherto confronted the student of radio-telegraphy. Thus the linear equations of the older theory must now be replaced by the non-linear equations necessary for the representation of finite vibrations. The equations are non-linear because the assembly of any triode or dynatron generator may be reduced to a combination of an oscillatory circuit (capacity and self-induction), and a conductor (triode or dynatron) for which Ohm's law is not obeyed. A more detailed analysis shows that interest must now centre round the solution of the equation

$$\frac{d^2v}{dt^2} + f(v)\frac{dv}{dt} + \omega^2 v = 0, \quad . \quad . \quad . \quad . \quad (1)$$

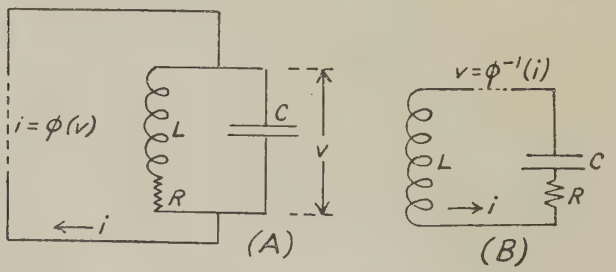
where v represents one of the variable electrical magnitudes (*e.g.*, current or potential difference), t the time, and ω is a constant. In the older equations the coefficient of $\frac{dv}{dt}$ is positive and constant, whereas in (1) the coefficient must be some function which assumes negative values for a certain range of values of v. In the simplest cases $f(v)$ is of the form $-\alpha + \gamma v^2$, where α and γ are positive constants. The amplitude of a generator represented by an equation of this type will automatically increase until a stationary value is

* Communicated by Sir J. Larmor, F.R.S.

reached. But often in practice $f(v)$ is of such a form (*e. g.*, $\alpha-\gamma v^2+\epsilon v^4$) that its value is positive when v is zero, but becomes negative when v is increased. In such cases oscillations will not start automatically, but if oscillations of amplitude greater than a certain critical value are temporarily induced in the system they are automatically maintained.

To illustrate the derivation of (1) and the determination of the appropriate values of the constants we may consider one or two examples. Almost all modern continuous-wave generators may be represented ideally by one of the two circuits shown in fig. 1, where the dotted lines represent some type of conductor not obeying Ohm's law and having a characteristic current-voltage relation expressed by $i=\phi(v)$, where i is the current through the conductor and v the difference of potential between its ends.

Fig. 1.



As examples of type A we may instance the ordinary triode and dynatron circuits, while the Duddell and Poulsen arcs are generators of type B. In both cases the relation between one of the variable electrical magnitudes and time t is represented by an equation exactly similar to (1). Thus in case A we may easily show that

$$\frac{d^2v}{dt^2}+\left[\frac{\mathrm{R}}{\mathrm{L}}+\frac{\phi'(v)}{\mathrm{C}}\right]\frac{dv}{dt}+\frac{v}{\mathrm{CL}}=0^*,$$

* More precisely the equation for this circuit is

$$\frac{d^2v}{dt^2}+\left[\frac{\mathrm{R}}{\mathrm{L}}+\frac{\phi'(v)}{\mathrm{C}}\right]\frac{dv}{dt}+\frac{v+\mathrm{R}i}{\mathrm{CL}}=0.$$

But in a practical case $\mathrm{R}i$ is small compared with v. If, however, a case arose in which this were not so, the equation could still be treated in the same way. We have purposely not dealt with the more general equation so as not to make the algebra unduly complicated.

while in case B the analogous equation is

$$\frac{d^2i}{dt^2}+\left[\frac{\mathrm{R}}{\mathrm{L}}+\frac{\dfrac{d}{di}\phi^{-1}(i)}{\mathrm{L}}\right]\frac{di}{dt}+\frac{i}{\mathrm{CL}}=0.$$

From these equations it will be seen at once that the condition for instability in case A is that the coefficient of $\frac{dv}{dt}$ should be negative when $v=0$. Similarly in case B the coefficient of $\frac{di}{dt}$ should be negative when $i=0$. Thus in case A we must have

$$\frac{\mathrm{CR}}{\mathrm{L}}+\phi'(0)<0,$$

and in case B

$$\mathrm{R}+\frac{1}{\phi'(0)}<0.$$

For instability in each case we must have a conductor with a falling current-voltage characteristic (*i. e.*, a so-called "negative resistance"). The derivation of a characteristic which illustrates the "negative resistance" effect of a triode oscillator has previously been given *. In the case of the arc the nature of the falling characteristic is well known.

In a recent paper † Dr. van der Pol and one of the writers gave an approximate solution of (1) which was, however, sufficiently accurate to account for the main features of the phenomenon of oscillation-hysteresis. In this approximate solution $f(v)$ was expressed as a power series, and use was made of the experimental fact, which is one quite familiar to practical workers, that the triode generator is singularly free from harmonics. Thus only the fundamental Fourier component of the current through the triode conductor was considered, the analysis being, in consequence, considerably simplified.

An elegant graphical solution of (1) has also been given by Dr. A. R. Robb ‡ for cases in which $f(v)$ is quite general. As, however, it is becoming more and more the custom in wireless practice to express the current-potential relations of

* Appleton & van der Pol, Phil. Mag. Ser. 6, vol. xlii. No. 248, p. 203, Aug. 1921.

† Appleton & van der Pol, "On a type of Oscillation-Hysteresis in a Simple Triode Generator," Phil. Mag. vol. xliii. p. 177, Jan. 1922.

‡ Robb, Phil. Mag. vol. xliii. p. 206, Jan. 1922.

triodes in the form of power series it seems desirable to treat (1) by purely analytical methods when $f(v)$ is expressed in this way, so that the amplitudes of the harmonics and the frequency of the generator can be accurately given It is, in this way, possible to see what factors are responsible for the remarkably sinusoidal nature of the oscillation, and also to determine precisely the variation of the oscillation frequency with variation of the triode and circuit parameters. Experimental data on this latter point have been published recently *.

We are thus concerned with the equation

$$\frac{d^2v}{dt^2} + f(v)\frac{dv}{dt} + \omega^2 v = 0, \quad . \quad . \quad . \quad . \quad (1)$$

where $f(v)$ is a power series in v and may be written

$$f(v) = -\alpha + \beta v + \gamma v^2 + \delta v^3 + \epsilon v^4 + \ldots, \quad . \quad . \quad (2)$$

the coefficients α, β, γ, δ, ϵ, etc., being small compared with ω. We shall assume that the series (2) is convergent for all values of v which occur in practice. It is obvious that $v=0$ is a solution of (1). This solution corresponds to a "stationary state" of the system. We shall show that in addition to this there are other "stationary states" given by periodic solutions of (1).

In determining these periodic solutions we shall introduce the condition that $v=0$ when $t=0$. This simply amounts to a suitable choice of the origin of time.

Let us write

$$\omega^2 = \omega_0^2(1 + \mu b_1 + \mu^2 b_2 + \mu^3 b_3 + \ldots + \mu^r b_r + \ldots), \quad (3)$$

and

$$\left.\begin{aligned} \frac{\alpha}{\omega_0} &= a_0\mu, \\ \frac{\beta}{\omega_0} &= a_1\mu, \\ \frac{\gamma}{\omega_0} &= a_2\mu, \\ \frac{\delta}{\omega_0} &= a_3\mu, \\ \frac{\epsilon}{\omega_0} &= a_4\mu, \quad \text{etc.} \end{aligned}\right\}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

* Eccles & Vincent, Proc. Roy. Soc. 96 A. p. 455, Feb. 3rd, 1920; and Vincent, Proc. Roy. Soc. 97 A. p. 191, 1920: see also a paper by Miss Leyshon, 'Radio Review,' vol. i. No. 10, p. 481, July 1920.

where μ is small. Let also

$$\omega_0 t = \tau. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

Thus, writing D for $\frac{d}{d\tau}$, (1) becomes

$$\mathrm{D}^2 v + \mu(-a_0 + a_1 v + a_2 v^2 + a_3 v^3 + a_4 v^4 \ldots + a_r v^r + \ldots)\mathrm{D}v$$
$$+ v(1 + \mu b_1 + \mu^2 b_2 + \ldots + \mu^r b_r + \ldots) = 0. \quad (6)$$

Let us assume as a solution

$$v = v_0 + v_1\mu + v_2\mu^2 + \ldots + v_r\mu^r + \ldots, \quad . \quad . \quad . \quad (7)$$

where v_0, v_1, v_2, etc. are periodic functions of τ with period 2π, all of which are zero when $\tau = 0$.

To determine v_0, v_1, v_2, etc. we substitute the expression (7) for v in equation (6) and equate coefficients of like powers of μ.

From the terms in μ^0 we obtain

$$(\mathrm{D}^2 + 1)v_0 = 0,$$

and therefore using the condition that $v_0 = 0$ when $\tau = 0$ we have

$$v_0 = \mathrm{A} \sin \tau, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

where A is a constant to be determined later.

From the terms in μ we obtain

$$(\mathrm{D}^2 + 1)v_1 + \mathrm{P}_1 = 0, \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

where

$$\mathrm{P}_1 = \mathrm{L}\frac{dv_0}{d\tau} + b_1 v_0, \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

and

$$\mathrm{L} = -a_0 + a_1 v_0 + a_2 v_0^2 + a_3 v_0^3 + a_4 v_0^4 + \ldots + a_r v_0^r + \ldots \quad (11)$$

We get from (8) and (11), writing $i = \sqrt{-1}$ as usual,

$$\mathrm{L} = l_0 + l_1(e^{i\tau} - e^{-i\tau}) + l_2(e^{2i\tau} + e^{-2i\tau})$$
$$+ l_3(e^{3i\tau} - e^{-3i\tau}) + l_4(e^{4\tau} + e^{-4i\tau})$$
$$+ \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad .$$
$$+ l_{2n}(e^{2ni\tau} + e^{-2ni\tau}) + l_{2n+1}(e^{(2n+1)i\tau} - e^{-(2n+1)i\tau})$$
$$+ \ldots., \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

where

$$\left.\begin{aligned}
l_0 &= -a_0 + \frac{1}{2}a_2A^2 + \frac{3}{8}a_4A^4 + \text{terms in } a_6A^6,\ a_8A^8,\ \text{etc.},\\
l_1 &= \frac{1}{2i}\left\{a_1A + \frac{3}{4}a_3A^3 + \text{terms in } a_5A^5,\ a_7A^7,\ \text{etc.},\right\}\\
l_2 &= -\frac{1}{4}a_2A^2 - \frac{1}{4}a_4A^4 + \text{terms in } a_6A^6,\ a_8A^8,\ \text{etc.},\\
l_3 &= -\frac{1}{8i}a_3A^3 + \text{terms in } a_5A^5,\ a_7A^7,\ \text{etc.},\\
l_4 &= \frac{1}{16}a_4A^4 + \text{terms in } a_6A^6,\ a_8A^8,\ \text{etc.},\\
l_5 &= \text{terms in } a_5A^5,\ a_7A^7,\ \text{etc.},\\
l_6 &= \text{terms in } a_6A^6,\ a_8A^8,\ \text{etc.},\\
l_7 &= \text{terms in } a_7A^7,\ a_9A^9,\ \text{etc.},
\end{aligned}\right\} \quad (13)$$

and generally

$$l_r = \text{terms in } a_rA^r,\ a_{r+2}A^{r+2},\ a_{r+4}A^{r+4},\ \text{etc.}$$

Again, from (8),

$$\frac{dv_0}{d\tau} = \frac{1}{2}A(e^{i\tau} + e^{-i\tau}) \quad . \quad . \quad . \quad . \quad . \quad (14)$$

From (10), (12), and (14) we obtain

$$P_1 = e^{i\tau}\left[\frac{1}{2}A(l_0 + l_2) + \frac{1}{2i}Ab_1\right] + e^{-i\tau}\left[\frac{1}{2}A(l_0 + l_2) - \frac{1}{2i}Ab_1\right]$$
$$+ \frac{1}{2}A\sum_{n=1}^{n=\infty}\left[q_{2n}(e^{2ni\tau} - e^{-2ni\tau}) + q_{2n+1}(e^{(2n+1)i\tau} + e^{-(2n+1)i\tau})\right],$$
$$. \quad . \quad . \quad (15)$$

where we have written

$$l_{r-1} + l_{r+1} = q_r. \quad . \quad . \quad . \quad . \quad . \quad (16)$$

In order that v_1, as determined from (9) may be periodic in τ with period 2π, the coefficients of $e^{i\tau}$ and $e^{-i\tau}$ in the expression (15) for P_1 must be zero, so that we must have

$$b_1 = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

and

$$l_0 + l_2 = 0. \quad . \quad . \quad . \quad . \quad . \quad . \quad (18)$$

The equation (18) determines the constant A.

Equation (15) now becomes

$$P_1=\frac{1}{2}A\sum_{n=1}^{n=\infty}\left[q_{2n}(e^{2ni\tau}-e^{-2ni\tau})+q_{2n+1}(e^{(2n+1)i\tau}+e^{-(2n+1)i\tau})\right],$$

and (9) gives . . . (15′)

$$v_1=\alpha_1e^{i\tau}+\beta_1e^{-i\tau}+\frac{1}{2}A\sum_{n=1}^{n=\infty}\left[\frac{q_{2n}}{(2n)^2-1}(e^{2ni\tau}-e^{-2ni\tau})\right.$$
$$\left.+\frac{q_{2n+1}}{(2n+1)^2+1}(e^{(2n+1)i\tau}+e^{-(2n+1)i\tau})\right]. \quad (19)$$

where α_1 and β_1 are constants which are arbitrary so far.

We may also write (19)

$$v_1=(\alpha_1+\beta_1)\cos\tau+i(\alpha_1-\beta_1)\sin\tau$$
$$+\frac{1}{2}A\sum_{n=1}^{n=\infty}\left[\frac{2q_{2n}i}{(2n)^2-1}\sin 2n\tau+\frac{2q_{2n+1}}{(2n+1)^2-1}\cos(2n+1)\tau\right].$$
. . . (19′)

From the terms in μ^2 we obtain

$$(D^2+1)v_2+P_2=0, \quad . \quad . \quad . \quad . \quad . \quad (20)$$

where

$$P_2=(-a_0+a_1v_0+a_2v_0^2+\ldots+a_rv_0^r+\ldots)\frac{dv_1}{d\tau}$$
$$+(a_1v_1+2a_2v_0v_1+3a_3v_0^2v_1+\ldots$$
$$ra_rv_0^{r-1}v_1+\ldots)\frac{dv_0}{d\tau}+b_2v_0,$$

giving

$$P_2=\frac{d}{d\tau}(Lv_1)+b_2v_0. \quad . \quad . \quad . \quad . \quad (21)$$

P_2 is a periodic function of τ with period 2π and may be written

$$P_2=\sum_{r=-\infty}^{r=+\infty}P_{2,r}\,e^{ri\tau}. \quad . \quad . \quad . \quad . \quad . \quad (22)$$

For v_2 as determined by (20) to be periodic in τ with period 2π we must have

$$\left.\begin{aligned} P_{2,1}&=0,\\ \text{and}\quad P_{2,-1}&=0.\end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad (23)$$

From (12) and (19) we find (using (16) and (18)) that in

v_1L the coefficients of $e^{i\tau}$ and $e^{-i\tau}$ are respectively,

$$l_0(\alpha_1-\beta_1)-\frac{1}{2}\mathrm{A}\sum_{n=2}^{n=\infty}\left[\frac{(-1)^n(q_n)^2}{n^2-1}\right]$$

and $$-l_0(\alpha_1-\beta_1)-\frac{1}{2}\mathrm{A}\sum_{n=2}^{n=\infty}\left[\frac{(-1)^n(q_n)^2}{n^2-1}\right].$$

We thus get

$$\left.\begin{aligned}\mathrm{P}_{2,1} &= il_0(\alpha_1-\beta_1)-\frac{1}{2}i\mathrm{A}\sum_{n=2}^{n=\infty}\left[\frac{(-1)^n(q_n)^2}{n^2-1}\right]+\frac{1}{2i}b_2\mathrm{A},\\ \mathrm{P}_{2,-1} &= il_0(\alpha_1-\beta_1)+\frac{1}{2}i\mathrm{A}\sum_{n=2}^{n=\infty}\left[\frac{(-1)^n(q_n)^2}{n^2-1}\right]-\frac{1}{2i}b_2\mathrm{A},\end{aligned}\right\}\quad(24)$$

and equations (23) become

$$\left.\begin{aligned}l_0(\alpha_1-\beta_1)-\frac{1}{2}\mathrm{A}\sum_{n=2}^{n=\infty}\left[\frac{(-1)^n(q_n)^2}{n^2-1}\right]-\frac{1}{2}b_2\mathrm{A}=0,\\ l_0(\alpha_1-\beta_1)+\frac{1}{2}\mathrm{A}\sum_{n=2}^{n=\infty}\left[\frac{(-1)^n(q_n)^2}{n^2-1}\right]+\frac{1}{2}b_2\mathrm{A}=0,\end{aligned}\right\}\quad(25)$$

giving

$$b_2=-\sum_{n=2}^{n=\infty}\left[\frac{(-1)^n(q_n)^2}{n^2-1}\right]\quad.\quad.\quad.\quad.\quad(26)$$

and

$$\alpha_1-\beta_1=0.\quad.\quad.\quad.\quad.\quad.\quad.\quad(27)$$

We now get from (19′)

$$v_1=(\alpha_1+\beta_1)\cos\tau+\frac{1}{2}\mathrm{A}\sum_{n=1}^{n=\infty}\left[\frac{2q_{2n}i}{(2n)^2-1}\sin 2n\tau+\frac{2q_{2n+1}}{(2n+1)^2-1}\cos(2n+1)\tau\right],\quad(19'')$$

and choosing $(\alpha_1+\beta_1)$, such that $v_1=0$ when $\tau=0$, we get

$$v_1=-\mathrm{A}\sum_{n=1}^{n=\infty}\left[\frac{q_{2n+1}}{(2n+1)^2-1}\right]\cos\tau+\mathrm{A}\sum_{n=1}^{n=\infty}\left[\frac{q_{2n}i}{(2n)^2-1}\sin 2n\tau+\frac{q_{2n+1}}{(2n+1)^2-1}\cos(2n+1)\tau\right].$$

$$.\quad.\quad.\quad(28)$$

We now get from (20)

$$v_2=\alpha_2e^{i\tau}+\beta_2e^{-i\tau}+\sum_{r=-\infty}^{r=+\infty}\left(\frac{\mathrm{P}_{2r}e^{ri\tau}}{r^2-1}\right),$$

where α_2 and β_2 are constants, arbitrary so far, which will be determined when we come to the consideration of the terms in μ^3.

In general, we get from the terms in μ^n,

$$v_n = \alpha_n e^{i\tau} + \beta_n e^{-i\tau} + \sum_{r=-\infty}^{r=+\infty} \frac{P_{nr}}{r^2-1} e^{ri\tau}, \quad . \quad . \quad (29)$$

where $P_{n,1}$ and $P_{n,-1}$ are zero.

The equation from which v_{n+1} is determined is

$$(D^2+1)v_{n+1} + P_{n+1} = 0, \quad . \quad . \quad . \quad . \quad (30)$$

where

$$\begin{aligned} P_{n+1} &= (-a_0 + a_1 v_0 + a_2 v_0^2 + \ldots + a_r v_0^r + \ldots)\frac{dv_n}{d\tau} \\ &\quad + (a_1 v_n + 2a_2 v_0 v_n + 3a_3 v_0^2 v_n + \ldots + r a_r v_0^{r-1} v_n + \ldots)\frac{dv_0}{d\tau} \\ &\quad + b_{n+1} v_0 + P_{n+1}^{(1)} \\ &= \frac{d}{d\tau}(Lv_n) + v_0 b_{n+1} + P_{n+1}^{(1)}. \end{aligned}$$

Here $P_{n+1}^{(1)}$ is an expression not involving v_n or b_{n+1} and may be determined from the previous stages of the work.

P_{n+1} is a periodic function of τ with period 2π and may written

$$P_{n+1} = \sum_{r=-\infty}^{r=+\infty} P_{n+1,r} e^{ri\tau}.$$

Since v_{n+1} as determined from (30) is to be periodic in τ with period 2π we must have

$$\begin{aligned} P_{n+1,1} &= 0 \\ \text{and} \quad P_{n+1,-1} &= 0, \end{aligned}$$

giving

$$\begin{aligned} l_0(\alpha_n - \beta_n) - \tfrac{1}{2} b_{n+1} A + R_n &= 0, \\ l_0(\alpha_n - \beta_n) + \tfrac{1}{2} b_{n+1} A + S_n &= 0, \end{aligned}$$

where R_n and S_n are expressions not involving α_n, β_n and b_{n+1}, and which are determined from the results of the previous stages of the work. These equations determine b_{n+1} and $(\alpha_n - \beta_n)$. $(\alpha_n + \beta_n)$ is then determined by using the conditions that $v_n = 0$ when $\tau = 0$.

We have now shown how periodic solutions of (1) may be obtained, there being one such solution for every value of A which satisfies (18).

It should be noted that we have not demonstrated the convergence of the series obtained. These series are power series in μ, and it is reasonable to assume * that they will be convergent for sufficiently small values of μ, and therefore for sufficiently small values of $\frac{\alpha}{\omega}$, $\frac{\beta}{\omega}$, $\frac{\gamma}{\omega}$, etc.

To obtain a convenient approximate result, let us neglect the terms in μ^2 and higher powers of μ in the expression (7) for v, and the terms in μ^3 and higher powers of μ in the expression (3) for ω^2.

We then have

$$v = v_0 + \mu v_1,$$
$$\omega^2 = \omega_0^2(1 + \mu^2 b_2).$$

In a practical case † it will often suffice to neglect all the coefficients in (2) except α and γ, in which case we have

$$f(v) = -\alpha + \gamma v^2. \quad . \quad . \quad . \quad . \quad . \quad (31)$$

Thus (18) becomes

$$-a_0 + \frac{1}{4} a_2 \mathrm{A}^2 = 0,$$

giving

$$\mathrm{A} = 2\sqrt{\frac{\alpha}{\gamma}}.$$

(28) becomes

$$v_1 = \frac{1}{8} a_0 \sqrt{\frac{\alpha}{\gamma}} \cos\tau - \frac{1}{8} a_0 \sqrt{\frac{\alpha}{\gamma}} \cos 3\tau,$$

and (26) becomes

$$b_2 = \frac{1}{8} a_0^2.$$

Thus the (approximate) solution is

$$v = 2\sqrt{\frac{\alpha}{\gamma}} \sin\omega_0 t + \frac{1}{8}\frac{\alpha}{\omega_0}\sqrt{\frac{\alpha}{\gamma}} \cos\omega_0 t - \frac{1}{8}\frac{\alpha}{\omega_0}\sqrt{\frac{\alpha}{\gamma}} \cos 3\omega_0 t,$$

where ω_0 is given by

$$\omega_0^2 = \omega^2 - \frac{1}{8}\alpha^2. \quad . \quad . \quad . \quad (32)$$

It is sometimes ‡ desirable, however, to retain all the coefficients up to ϵ in (2) so that

$$f(v) = -\alpha + \beta v + \gamma v^2 + \delta v^3 + \epsilon v^4. \quad . \quad . \quad . \quad (33)$$

* This will be proved in a subsequent paper.
† Appleton & van der Pol, *loc. cit.* p. 182.
‡ Appleton & van der Pol, *loc. cit.* p. 183.

In this case (18) becomes

$$\epsilon A^4 + 2\gamma A^2 - 8\alpha = 0,$$

giving

$$A = \sqrt{-\frac{\gamma}{\epsilon} \quad \sqrt{\frac{\gamma^2}{\epsilon^2} + \frac{8\alpha}{\epsilon}}} \quad \ldots \quad (34)$$

Corresponding to each of these two values of A there is a periodic solution. In this case we have

$$q_2 = \frac{1}{2i}\left(a_1 A + \frac{1}{2} a_3 A^3\right),$$

$$q_3 = -\frac{1}{4} a_2 A^2 - \frac{3}{16} a_4 A^4,$$

$$q_4 = -\frac{1}{8i} a_3 A^3,$$

$$q_5 = \frac{1}{16} a_4 A^4,$$

$$q_6 = q_7 = q_8 = \ldots = 0,$$

(28) becomes

$$v_1 = A\left[\frac{1}{32} a_2 A^2 + \frac{1}{48} a_4 A^4\right] \cos \tau$$

$$+ \frac{1}{6} A\left(a_1 A + \frac{1}{2} a_3 A^3\right) \sin 2\tau - \frac{1}{32} A\left(a_2 + \frac{3}{4} a_4 A^4\right) \cos 3\tau$$

$$- \frac{1}{120} a_3 A^4 \sin 4\tau + \frac{1}{384} a_4 A^5 \cos 5\tau,$$

and (26) becomes

$$b_2 = \frac{1}{12}\left(a_1 A + \frac{1}{2} a_3 A^3\right)^2 + \frac{1}{128}\left(a_2 A^2 + \frac{3}{4} a_4 A^4\right)^2$$

$$+ \frac{1}{960} a_3^2 A^6 + \frac{1}{6144} a_4^2 A^8,$$

so that the (approximate) solutions are

$$\left.\begin{aligned} v = {} & \mathrm{A}\sin\omega_0 t + \frac{1}{16}\mathrm{A}\left(\frac{1}{2}\frac{\gamma}{\omega_0}\mathrm{A}^2 + \frac{1}{3}\frac{\epsilon}{\omega_0}\mathrm{A}^4\right)\cos\omega_0 t \\ & + \frac{1}{6}\mathrm{A}\left(\frac{\beta}{\omega_0}\mathrm{A} + \frac{1}{2}\frac{\delta}{\omega_0}\mathrm{A}^3\right)\sin 2\omega_0 t \\ & - \frac{1}{32}\mathrm{A}\left(\frac{\gamma}{\omega_0} + \frac{3}{4}\frac{\epsilon}{\omega_0}\mathrm{A}^4\right)\cos 3\omega_0 t \\ & - \frac{1}{120}\frac{\delta}{\omega_0}\mathrm{A}^4\sin 4\omega_0 t + \frac{1}{384}\frac{\epsilon}{\omega_0}\mathrm{A}^5\cos 5\omega_0 t, \end{aligned}\right\} \quad (32')$$

where ω_0 is given by

$$\left.\begin{aligned} \omega_0^2 = {} & \omega^2 - \frac{1}{12}\left(\beta\mathrm{A} + \frac{1}{2}\delta\mathrm{A}^3\right)^2 - \frac{1}{128}\left(\gamma\mathrm{A}^2 + \frac{3}{4}\epsilon\mathrm{A}^4\right)^2 \\ & - \frac{1}{960}\delta^2\mathrm{A}^6 - \frac{1}{6144}\epsilon^2\mathrm{A}^8, \end{aligned}\right\}$$

and A has either of the values (34).

We have previously seen that A is determined by the equation

$$l_0 + l_2 = 0,$$

and it is easy to see further that the general terms in the expressions for l_0 and l_2 are respectively

$$\frac{1}{2^{2n}}\frac{\lfloor 2n}{(\lfloor n)^2}a_{2n}\mathrm{A}^{2n},$$

and

$$-\frac{1}{2^{2n}}\frac{\lfloor 2n}{\lfloor n-1\ \lfloor n+1}a_{2n}\mathrm{A}^{2n}.$$

The equation $l_0 + l_2 = 0$ thus becomes

$$-a_0 + \sum_{n=1}^{n=\infty}\frac{\lfloor 2n\, a_{2n}\mathrm{A}^{2n}}{2^{2n}\lfloor n\ \lfloor n+1} = 0. \quad . \quad . \quad . \quad (35)$$

This is an equation determining A, and to every root there corresponds a periodic solution of (1) representing a "stationary state."

The condition for stability of these periodic solutions has been given in a previous paper *. It is (in the present notation)

$$-a_0 + \sum_{n=1}^{n=\infty}\frac{\lfloor 2n}{2^{2n}(\lfloor n)^2}a_{2n}\mathrm{A}^{2n} > 0. \quad . \quad . \quad . \quad (36)$$

* Appleton & van der Pol, *loc. cit.*, equation (10), p. 182.

Equations (32′), (34), and (36) therefore give us the information we require in practice regarding the amplitude, stability, and frequency of the oscillation in any stationary state. Equation (32′) also enables us to determine the magnitude of the harmonics in any particular case.

Much experimental work has recently been carried out using the triode oscillator as a reference standard of frequency, and it is of interest to note that the variation of frequency with the triode parameters found in practice is in excellent agreement with that suggested by (32′). Thus the frequency is always found to be less than ω, the difference increasing as the amplitude A is increased.

It is also possible * to realize physically three of the "stationary states" indicated by the solution given above, of which one is given by $A = 0$ and the others by (34). Such "stationary states" are utilized in the so-called "trigger" relays, in which a transient signal causes the oscillator to pass from the "stationary state" $A = 0$ to that of the first value of (34). The second value of A in (34), which represents an unstable "stationary state," may be identified with the so-called "threshold" value of the signal oscillation necessary for the relay to function.

Note (1).—It is of interest to notice that we can easily construct (mathematically at any rate) examples in which the equation (35) has an enumerable infinity of real roots. For instance, we may take

$$f(v) = -\mu \cos v \dagger,$$

so that

$$\left.\begin{aligned} a_0 &= 1, \\ a_{2n} &= \frac{(-1)^{n+1}}{\underline{|2n}}, \qquad (n > 0) \\ a_{2n+1} &= 0. \end{aligned}\right\}$$

If we multiply (35) by $\frac{1}{2}A$ it becomes

$$\sum_{n=0}^{n=\infty} \frac{(-1)^{n+1} A^{2n+1}}{2^{2n+1} \underline{|n} \, \underline{|n+1}} = 0,$$

that is

$$J_1(A) = 0,$$

where, as usual, J_1 denotes the Bessel function of order 1.

* Appleton & van der Pol, *loc. cit.*

† This example arose out of a suggestion made by Mr. D. P. Dalzell, of St. John's College, Cambridge.

It is well known that this equation has an enumerable infinity of real roots.

Furthermore with these values of the a's (36) becomes

$$1+\sum_{n=1}^{n=\infty}\frac{(-1)^n A^{2n}}{2^{2n}(\underline{n})^2}<0,$$

that is

$$J_0(A)<0.$$

It is well known that $J_0(A)=0$ has an enumerable infinity of real roots, and that between every two of these there lies one, and only one, root of $J_1(A)=0$, so that the periodic solutions in this case are alternately stable and unstable.

This example suggests the possibility of the existence of physical systems, governed by the ordinary laws of Newtonian Mechanics, and possessing an enumerable infinity of alternately stable and unstable stationary states.

Note (2).—In the above work we have been concerned with the determination of the periodic solutions of (1) which give the stationary states of the system. These solutions are of mathematical interest as they are of a type rather different from the periodic solutions of dynamical equations which have been discussed by Poincaré. Their relation to the ordinary theory of periodic solutions will be discussed in a later paper.

We wish to express our gratitude to Professor Sir Joseph Larmor and Professor H. F. Baker for the kind interest they have taken in the preparation of this paper.

XLIV. *On Restricted Movements of Molecules at very low pressures.*

To the Editors of the Philosophical Magazine.

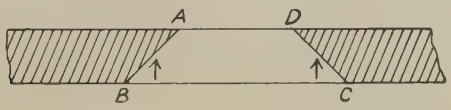
Gentlemen,—

In the June Philosophical Magazine, under the title "Restricted Movements of Molecules at very low pressures," Arthur Fairbourne very interestingly sets forth a method for the possible experimental demonstration of a limit of applicability of the Second Law of Thermodynamics. In this paper, however, he seems to have overlooked a possibility of great importance for the mechanical realization of this aim. Fairbourne shows that tapered vessels, open at both ends, whose dimensions are made smaller than the free path of many of the molecules of the gas employed, may be expected to cause an appreciable flow of gas emerging from

the larger end of the vessel. He further proposes the mounting of a small vane within or below this opening for the detection of the expected motion in low-pressure gases.

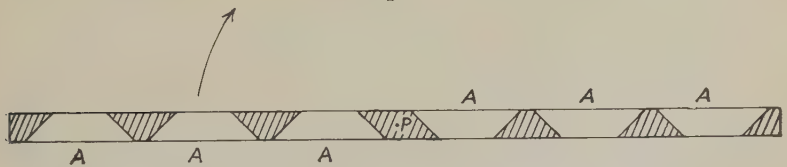
Since the flow in the gas is entirely the result of impacts of individual gas molecules against the walls of the vessel, it follows that there must result a corresponding reaction against the vessel itself opposite in direction to the gas-flow. That is, a pressure having an unbalanced component in the direction of the small opening must be exerted against the inner walls of the vessel. Let us attach this vessel to a flat plate so that it becomes a tapered aperture through the plate, as in fig. 1, instead of an independent vessel.

Fig. 1.



Evidently if we mount the plate as a vane suspended by a quartz fibre or other sufficiently delicate pivot, we should be able to detect a motion of the plate. The effect may be greatly multiplied by perforating the plate with a large number of tapered apertures, arranged as shown at A, A in fig. 2. If a vane of this type were delicately suspended in a

Fig. 2.



closed gas-filled vessel and the pressure gradually reduced, we should finally reach a point where the molecule paths have grown in length until the selective action becomes appreciable. Then we may expect the vane to start rotating about the pivot P in the direction of the arrow, and to maintain this motion at the expense of the heat in the gas so long as the necessary conditions are present. Obviously this apparatus is capable of far greater delicacy than is Fairbourne's suggested vane, which could utilize a portion only of the force resulting from a single aperture.

Yours faithfully,

Scarsdale, N.Y.
August 25th, 1922.

HAVILAND H. PLATT.

XLV. *The Specific Heats of Nitrous and Nitric Oxides.* *By* Prof. J. R. Partington, *D.Sc., and* W. G. Shilling, *M.C., M.Sc.**

THE following investigation was undertaken with the object of providing reasonably accurate data for the values of the specific heats of nitrous oxide and of nitric oxide. Nitrous oxide is of special interest from the standpoint of the Lewis-Langmuir theory when compared with carbon dioxide, since the two gases have identical external electronic structures. Their respective physical constants have, in very many cases, almost identical values. Nitric oxide is similar to carbon monoxide and to nitrogen, but the analogy is not so complete as in the case of nitrous oxide and carbon dioxide. This is only to be expected, since nitrogen and carbon monoxide have ten electrons in the outer shell, whereas nitric oxide has eleven.

The results previously obtained for nitrous oxide are so discordant that it is impossible to deduce any mean value from them. The differences may be largely attributed to the impurity of the gas used. Masson † determined the ratio of the specific heats by determining the frequencies with which a reed vibrated in the different gases. His observed value for nitrous oxide was $\kappa = 1{\cdot}28132$. A value of $\kappa = 1{\cdot}285$ was obtained by Cazin ‡. He employed the adiabatic expansion method, using as the containing vessel a large globe of 60 litres capacity. Regnault § measured the specific heat at constant pressure by his calorimeter method. He obtained a value, at 105° C. of $Cp = 9{\cdot}94$ gm. cals. Employing Berthelot's equation of state, this leads to a value $\kappa = 1{\cdot}253$. Although Regnault estimated the amount of nitrogen present as an impurity, he did not consider his results as being very accurate. A method similar in principle to that afterwards used by Masson was employed by Dulong ‖. Assuming the velocity of sound in free air at 22° C. to be 333 m./sec., he found a value $\kappa = 1{\cdot}343$. His experimental figures, when re-calculated using Berthelot's equation and modern physical constants, give $\kappa = 1{\cdot}332$. A value of $\kappa = 1{\cdot}3106$ for nitrous

* Communicated by the Authors.

† *Ann. de Chim. et de Phys.* (3) liii. p. 257 (1858).

‡ *Ann. de Chim. et de Phys.* lxvi. p. 206 (1862); *cf.* Phil. Mag. (4) xl. p. 209 (1870).

§ *Mém. de l'Académie*, vol. xxvi. p. 135 (1862).

‖ *Ann. de Chim. et de Phys.* (2) xli. p. 113 (1892).

oxide was obtained by Wüllner * by the dust-figure method. The above value, after a small correction for frequency and for inaccurate density values employed by Wüllner, gives $\kappa = 1{\cdot}323$. The only modern figures are those of Mercer, Schweikert, and those given by Heuse. Mercer † employed a platinum resistance thermometer to measure the instantaneous fall of temperature corresponding to a rapid fall of pressure. His apparatus was similar to that of Makower ‡, except that he used a very small vessel. He attempted to correct for the large influence which conduction and convection would have in this case. A correction was also applied for the 2·6 per cent. of oxygen in the nitrous oxide. This was assumed to be present as air (*i. e.* 13 per cent. impurity), and the correction was made by means of an equation which, as Stevens § had already shown, does not hold good experimentally. The above corrections, together with one for a defective thermometer, increased Mercer's observed value of κ for nitrous oxide from 1·229 to 1·261, a result which appears somewhat uncertain owing to the number and magnitude of the corrections necessary. Schweikert ‖ reverted to a slight modification of the original Kundt method. His results give $\kappa = 1{\cdot}289$ at 0° C. The most recent result is that of Heuse ¶, who employed the constant-flow calorimeter method of Callendar and Barnes. This method appears always to give results for κ which are somewhat lower than those obtained by other methods **. The value for nitrous oxide given by Heuse is $\kappa = 1{\cdot}277$ at 0° C.

It will be seen that the above results, varying from $\kappa = 1{\cdot}25$ to $\kappa = 1{\cdot}32$, leave much doubt as to the correct value.

In the experiments described below, the method employed was that of Kundt as modified by Behn and Geiger. The method has been described in a recent paper ††, so that a reference to the modifications introduced will be sufficient. The gas-tube was now fitted with a side tube attached centrally to it and carrying a tap and one-half of a ground-glass joint. This side tube had no effect on the

* Wied. *Ann.* iv. p. 321 (1878).
† Proc. Phys. Soc. Lond. xxvi. p. 155 (1914).
‡ Phil. Mag., Feb. 1903.
§ Diss. Heidelberg, 1900.
‖ *Ann. Phys.* (4) xlviii. p. 593 (1915).
¶ *Ann. Phys.* (4) lix. p. 86 (1919).
** Partington, Proc. Roy. Soc. A, vol. c. p. 47 (1921).
†† Partington & Cant, Phil. Mag. (6) xliii. p. 369 (1922).

vibration of the tube, since it passed through a slot cut in the wooden clamp. The great advantages of this fitting are that it is easily connected to the filling apparatus and the tube can be emptied and refilled as often as desired without cleaning and redrying; its ends can also be blown perfectly hemispherical. In the case of nitrous oxide the heat used in sealing-off would have decomposed some of the gas, had the previous method of closing the tube been used. Nitrous oxide begins to decompose at 520° C.*, and the decomposition is complete at 900° C.†. The tap attached to the side tube had a specially large bore of 4 mm. to facilitate washing and cleaning, and the barrel was sealed in with wax during actual use to prevent the possibility of its shaking loose by the vibration of the tube. The diagram of the apparatus (fig. 1) shows the complete arrangement.

Nearly all previous work on nitrous oxide has been vitiated by the use of impure gas. No account seems to have been taken of the fact that the gas made by heating ammonium nitrate inevitably contains nitrogen ‡, the percentage of which varies from 2 per cent. upwards, according to the care taken in heating the ammonium nitrate. Reliquifying the gas in liquid air and allowing the nitrogen to boil off § seems to be the only satisfactory method of eliminating this impurity. The commercial liquid which is stored at a pressure of 70–75 atmospheres, in cylinders, will contain this nitrogen in solution.

In the first series of experiments the technical gas from a cylinder was used. It was washed in solutions of ferrous sulphate and of potassium hydroxide. The nitrogen present was estimated by dissolving out the nitrous oxide in air-free water at 2° C. after the experiment. Pure nitrous oxide was used in all other experiments. It was made ‖ by allowing a concentrated solution of sodium nitrite in air-free water to drop on to a solution of hydroxylamine hydrochloride also in air-free water. The generating apparatus, which could be completely evacuated, is shown on the left of fig. 1. The gas was passed through a 50 per cent. solution of sodium hydroxide and then dried by means of

* Berthelot, *C. R.* lxxvii. p. 1451 (1873).

† Meyer and Langen, *Pyrochem. Untersuch.*. Brunswick, p. 65 (1885)

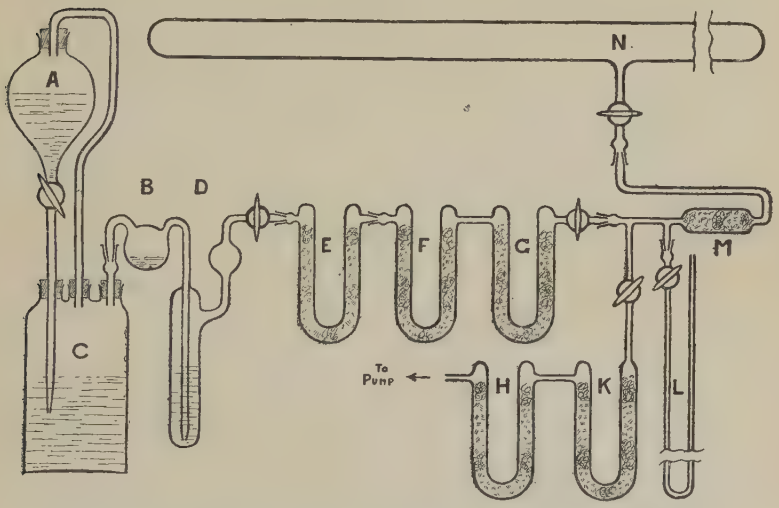
‡ Regnault, *Mém. de l'Acad.* vol. xxvi. p. 135 (1862); confirmed by Saunders, J. C. S. p. 698 (1922).

§ Villard, *C. R.* cxviii. p. 1096 (1894).

‖ Meyer, Wied. *Ann.* clxxv. p. 141 (1875).

calcium chloride and phosphorus pentoxide. The whole apparatus was made to hold a vacuum for several hours previous to filling the tubes, thus ensuring the absence of any leakage. When the gas-tube was filled with a pure specimen of the gas, the tap was simply closed and sealed in with wax. The tube was then ready for the experiment.

Fig. 1.



A contains sodium nitrite solution for nitrous oxide, potassium ferrocyanide, and potassium nitrite solutions for nitric oxide; B is a trap for any liquid sucked back from D; C contains hydroxylamine hydrochloride solution for nitrous oxide, dilute acetic acid for nitric oxide; D contains 50 per cent. potassium hydroxide solution to eliminate any traces of chlorine, carbon dioxide, etc.; E is a calcium-chloride drying-tube for nitrous oxide, solid potassium hydroxide for nitric oxide; F and G are phosphorus pentoxide drying-tubes; L is the manometer; M a phosphorus pentoxide drying-tube; and N is the gas-tube.

Effect of moisture in the air in the comparison tube.

The value of κ for air which was used as the standard was taken to be 1·403 *. This value applies to dry air, free from carbon dioxide. Keutel † had found that the

* Partington, Proc. Roy. Soc. A, vol. c. (1921).
† Inaug. Diss. Berlin (1910).

error introduced by the use of ordinary air as the standard was negligible. It was, however, thought desirable to test this point. A series of experiments was therefore undertaken to compare the wave-lengths obtained in "pure" and in ordinary air. The results showed clearly that it is necessary, under the conditions obtaining in our laboratory, to take pure air as the standard.

In the first series of experiments, waves were produced and measured in the open air-tube filled with ordinary air. Air, purified by forcing it slowly over broken stick potassium hydroxide followed by two drying-tubes containing phosphorus pentoxide, was then passed into the air-tube for a period of 6 to 8 hours. Dust-figures were then produced in the fresh powder which had been introduced along the tube. The temperature remained constant throughout. Table I. gives the results obtained. In the first of the series the relative humidity was not measured.

Table I.

Wave-lengths in Dry and Moist Air.

Date.	Moist air.	Dry air.	Temp., ° C.	Humidity.
18.1.22	7·244	7·201	15·6	——
20.1.22	7·233	7·201	15·4	——
23.1.22	5·840	5·819	12·4	——
24.1.22	5·822	5·814	13·2	——
25.1.22	5·849	5·829	15·5	0·78 } Wet and dry bulb.
30.1.22	8·259	8·188	11·5	0·798 }
31.1.22	8·286	8·188	11·5	0·776 }
2.2.22	8·308	8·255	12·0	0·85 chem. method.
6.2.22	Identical waves.		7·0	0·38 „ „
14.2.22	9·016	9·015	12·0	0·58 „ „

Measurements of the humidity were taken by the chemical method for the last three of the series. The wet- and dry-bulb readings are only comparable under standard conditions and are of little use for this type of work. The more expeditious method of keeping a sealed tube filled with pure air was afterwards substituted for the somewhat tedious method described above. The ratio (*vel. in dry air*) / (*vel. in moist air*) was determined for the conditions of each experiment with other gases. By this method the wave-lengths in nitrous and nitric oxides were compared with that of pure dry air for every experiment.

The difference obtained by using pure air usually altered the value of κ by amounts which were certainly greater than the limits of error of the experiment.

Stevens * attempted to correct the value of Cp/Cv for moist air by a simple proportion on the ratio Cp/Cv for each of the gases concerned. But this could only be done if both gases were ideal. A simple proportion on Cv would be more accurate. The quantitative relations for gas mixtures have, unfortunately, not yet been investigated. Work in this direction will shortly be undertaken in this laboratory. Schweikert † deduced a formula for reducing values in moist air at $t°$ C. to dry air at 0° C. But the formula holds only if Cp/Cv can be assumed to be constant for any temperature or gas mixture. This assumption is wrong theoretically and is not substantiated by any of the experimental evidence so far available. Since the experimental data at present available are not sufficient to test any formula which might be deduced, the method of correction by direct experiment, as described, was used throughout the present work.

Experimental Results.

Table II. gives the results obtained for nitrous oxide. Each experiment was carried out with a fresh sample of the pure gas, and the wave-lengths given are the mean values from a series of measurements. The first result is from a sample of the commercial gas from a cylinder. The nitrogen contained in it was estimated, as described, after the experiment, and a correction made on the value of Cv. The corrected value of the mean wave-length for this experiment has been calculated from the corrected value of Cv. A mean content of 8 per cent. of nitrogen was found. Tables III. to V. give a complete set of measurements for one experiment. In these tables the first column gives the number of half wave-lengths measured. The distances given under the headings A and B are the distances A′D′, A′E′, A′F′, and BE, BF, etc. given in the lower diagram of fig. 2 in the paper of Partington and Cant already mentioned. Where two or three sets of readings are given, the zero was changed for the second and third sets.

* Diss. Heidelberg, 1900, pp. 29 *et seq.*

† *Ann. Phys.* xlviii. p. 598 (1914).

Table II.

Wave-lengths in Air and Nitrous Oxide.

Tube 1.

No. of exp.	Dry air. $\lambda/2$ corr.	N_2O. $\lambda/2$.	κ'.	ϕ.	κ.	Temp., ° C.
1.	7·775	6·023	1·279	1·0121	1·294	12·8
2.	7·052	5·471	1·283	1·0120	1·298	13·5
3.	7·053	5·461	1·278	1·0121	1·293	13·2
4.	6·752	5·234	1·280	1·0122	1·296	12·2
5.	6·750	5·232	1·280	1·0121	1·295	12·8
6.	7·050	5·475	1·286	1·0121	1·301	12·8
Means...	7·072	5·483	1·281	1·0121	1·296	12·9
Tube 2.						
1.	8·155	6·308	—	—	—	11·5
2.	8·224	6·361	—	—	—	12·0
3.	8·690	6·690	—	—	—	11·2
Means...	8·356	6·453	1·272	1·0122	1·287	11·6

The discrepancy between tubes 1 and 2 in Table II. is explained later. The value of ϕ, the correction for the deviation of the gas from the ideal state, was calculated from Berthelot's equation, as in the paper of Partington and Cant.

Table III.

Series of Measurements for one Determination.
Temp. 13°·5 C.

To find the ratio Dry air/Moist air.

1. Dry air in sealed tube :— (all in cms.)

No.	A.	B.	Mean.	$\lambda/2$.
5.	24·9 25·0	25 25·2	25·025	5·005
6.	30·0 30·0	30·1 30·2	30·075	5·012
7.	35·0 35·1	35·1 35·1	35·075	5·011
8.	40·05 40·0	40·1 40·1	40·062	5·008
9.	44·9 44·9	45·0 45·1	49·475	4·997
10.	49·8 49·9	50·0 50·0	49·925	4·992
11.	55·0 55·0	54·9 55·0	54·975	4·998
			Mean	5·003

Table III. (*cont.*).

2. Moist air in open tube :—

No.	A.	B.	Mean.	λ/2.
	35·0	35·3		
	35·15	35·2	35·102	5·023
8.	39·8	40·3		
	40·1	40·1	40·075	5·009
9.	45·2	45·3		
	45·3	45·05	45·212	5·023
10.	50·2	50·2		
	50·2	50·1	50·175	5·018
	50·2	50·15		
11.	55·2	55·3		
	55·2	55·1	55·20	5·018
12.	60·2	60·3		
	60·3	60·2	60·238	5·020
13.	65·2	65·2		
	65·2	65·1	65·175	5 017
	65·15	65·2		
			Mean	5·018

Table IV.

Nitrous Oxide tube, 13°·5 C. :—

No.	A.	B.	Mean.	λ/2.
6.	32·7	33·0		
	32·7	33·0	32·825	5·471
	32·7	32·9		
7.	38·2	38·5		
	38·1	38·4	38·275	5·468
	38·2	38·25		
8.	43·5	44·0		
	43·6	43·9	43·758	5·470
	43·7	43·85		
9.	49·2	49·3		
	49·0	49·45	49·275	5·475
	49·2	49·5		
10.	54·5	54·9		
	54·6	55·0	54·733	5·473
	54·7	54·7		
11.	60·15	60·5		
	60·1	60·5	60·226	5·478
	60·1	60·25		
12.	65·6	65·7		
	65·6	65·7	65·65	5·471
13.	71·15	71·25		
	70·9	71·2	71·175	5·475
14.	76·55	76·6	76·575	5·470
15.	81·8	82·0		
	81·9	82·1	82·00	5·467
	82·0	82·2		
16.	87·35	87·4	87·375	5·461
17.	92·9	93·1		
	92·85	93·15	93·00	5·470
			Mean	5·471

TABLE V.

Air Comparison tube at 13°·5 C. :—

No.	A.	B.	Mean.	λ/2.
	35·4	35·4		
5.	35·4	35·5	35·425	7·085
	42·5	42·4		
6.	42·4	42·5	42·450	7·075
	49·5	49·5		
7.	49·5	49·55	49·512	7·073
	56·6	56·6		
8.	56·55	56·6	56·588	7·073
	63·6	63·6		
9.	63·6	63·8	63·650	7·072
	70·6	70·7		
10.	70·65	70·7	70·663	7·066
	77·7	77·7		
11.	77·65	77·7	77·687	7·063
	84·7	84·7		
12.	84·8	84·85	84·862	7·072
			Mean	7·072

This, when corrected for *dry* air at 13°·5 C., becomes :

$$\frac{7{\cdot}072 \times 5{\cdot}003}{5{\cdot}018} = 7{\cdot}052 \text{ cms.}$$

Nitric Oxide.

The method employed for nitric oxide was similar to that used for nitrous oxide, the only alteration being the substitution of the generating apparatus by a larger one. This was rendered necessary by the comparatively low solubility of the substances employed. Pure nitric oxide was prepared by dropping a solution of potassium ferrocyanide and potassium nitrite into dilute acetic acid. The lower vessel, containing the acetic acid, was provided with a small dropping funnel and an exit tube, closed by a tap, so that it could be emptied and recharged with acid without disconnecting any of the apparatus. The first drying-tube, which for nitrous oxide contained calcium chloride, was replaced by one containing broken stick potassium hydroxide. The mercury in the manometer was protected by a layer of strong sulphuric acid.

The only results previously obtained for nitric oxide

appear to be those of Regnault, Masson, and Heuse. Regnault* first prepared the gas by the action of nitric acid on copper, but afterwards substituted a method in which he reduced potassium nitrate by means of an acid solution of ferrous chloride. This method, as he states, gives almost pure nitric oxide. His results, at a mean temperature of 88°·8 C., lead to the values: $Cp = 7{\cdot}22$, $Cv = 5{\cdot}23$, $Cp/Cv = \kappa = 1{\cdot}380$. Masson †, using the method described under nitrous oxide, obtained a value $\kappa = 1{\cdot}414854$. The values $Cp = 7{\cdot}25$, $Cv = 5{\cdot}25$, $Cp/Cv = 1{\cdot}380$ were obtained by Heuse ‡. He prepared the gas by the action of nitric acid on copper, and purified it by absorption in ferrous sulphate solution and expulsion by subsequent warming.

The results obtained in the present series of experiments are tabulated below (Table VI.).

TABLE VI.

Tube 1.

No. of exp.	Dry air. λ.	NO. λ.	κ'.	ϕ.	κ.	Temp. ° C.
1.	13·342	13·050	1·389	——	——	6·0
2.	13·352	13·094	1·396	——	——	6·5
3.	13·398	13·104	1·390	——	——	8·0
4.	13·404	13·120	1·391	——	——	8·3
5.	13·390	13·118	1·393	——	——	8·3
6.	13·360	13·098	1·396	——	——	8·0
7.	13·432	13·138	1·390	——	——	8·4
Means ...	13·382	13·103	1·392	1·00184	1·394	7·6

Tube 2.

	$\lambda/2$.	$\lambda/2$.				
1.	8·356	8·567	——	——	——	6·8
2.	8·394	8·622	——	——	——	8·3
Means ...	8·375	8·594	1·379	1·00184	1·381	7·5

The discrepancy between tubes 1 and 2 is explained later.

* *Mém. de l'Académie*, vol. xxvi. p. 137 (1862).
† Phil. Mag. (4) xiii. p. 533 (1857).
‡ *Ann. Phys.* (4) lix. p. 86 (1919).

The Tube Correction.

It has been shown, both theoretically and experimentally, that the velocity of sound, u, in a gas contained in a relatively small tube, is somewhat smaller than that in the free gas. To obtain the true velocity, the corrections usually applied are: (i.) for the effect of the yielding of the walls of the tube *, and (ii.) for the effect of the diameter of the tube †. The first correction, in the case of gases, has an influence which is quite negligible unless the tube wall is very thin. When applied to the results given in Table II. it gives a value $u^2_{\text{true}} = u^2_{\text{observed}} \times 1{\cdot}000095$—a correction quite outside the limits of error of the experiment. A modified form of the second correction ‡, when applied to the results in Table II., gives a result identical with that already given. The calculated value of Kirchhoff's correction does not agree with that found experimentally §. The experimental value is always greater, but by a very uncertain amount. The constant γ in Kirchhoff's formula is dependent on the viscosity and thermal conductivity of the gas contained in the tube. No account is taken of the thermal properties of the tube, or of the nature of its inner surface. Stürm ‖ has shown that these factors affect considerably the velocity of sound in a gas in a tube. The constant γ, if it is to be of any value, must include terms relating to the tube as well as to the gas. Hence the method of eliminating the tube constant by employing two or more tubes of different radii is not strictly accurate. It assumes a value of γ which is constant for all the tubes—a condition which is extremely difficult to realize experimentally.

The air tube used in the experiments described was a heavy thick-walled (4 mm.) tube, whilst gas tube 1 was much lighter. Gas tube 2 was a very light, thin tube. Unless the tube correction is eliminated between these tubes, measurements taken with them are not comparable. Since this comparison is the fundamental principle of this method of experiment, the elimination of the

* Lamb, 'Dynamical Theory of Sound,' 1910, p. 174.

† Kirchhoff, *Pogg. Ann.* cxxxiv. p. 177 (1868).

‡ Fürstenau, *Ann. Phys.* (4) xxvii. p. 735 (1908); Jeans, 'Dynamical Theory of Gases,' 2nd edit. p. 315.

§ Schneebeli, *Pogg. Ann.* cxxxvi. p. 296 (1869); Seebeck, *op. cit.* cxxxix. p. 104 (1870); Kayser, Wied. *Ann.* ii. p. 235 (1877); Müller, *Ann. Phys.* xi. p. 331 (1903).

‖ *Ann. Phys.* xiv. p. 822 (1904).

effect of the tube used is very essential. The experimental results of Table VII. show this to be the case. To calculate the experimental value of the constant γ, the frequency must be known. The difficulty of determining accurately the frequency of the short shrill note emitted by the tube when rubbed, is apparent. It was therefore

TABLE VII.

Comparison of the gas tubes with the standard air tube.

Tube 1.

	$\lambda/2$ air tube.	$\lambda/2$ gas tube.
	6·869 cm.	6·798 cm.
	6·871 „	6·836 „
	6·871 „	6·869 „
	6·862 „	6·867 „
	6·861 „	6·861 „
	6·872 „	6·849 „
	6·861 „	6·860 „
	6·865 „	
Means...	6·866 cm.	6·849 cm.

Ratio = 6·866/6·849 = 1·00248 = the factor for tube 1.

Tube 2.

	8·769 cm.	8·721 cm.
	8·750 „	8·705 „
	8·754 „	8·694 „
	8·764 „	8·698 „
	8·766 „	8·699 „
	8·766 „	8·711 „
	8·760 „	
	8·764 „	
Means...	8·762 cm.	8·705 cm.

Ratio = 8·762/8·705 = 1·0065 = the factor for tube 2.

decided to eliminate the tube correction instead of attempting to find its absolute value. To do this, all measurements were referred to the large air tube as a standard. The gas and air tubes were both filled with pure dry air, and the waves produced simultaneously in each were measured. The results are given in Table VII. The ratio $\lambda_{\text{air tube}}/\lambda_{\text{gas tube}}$, with dry air in each, was always greater than unity and a different ratio was found for the two

different gas tubes. If the wave-lengths obtained when the gas tubes were filled with nitrous or nitric oxides are now multiplied by the factor for the tube employed, the resulting wave-lengths will be strictly comparable with those for the air in the air tube. In the corrected results given in Tables VIII. and IX. it will be seen that the discrepancies between the two series of results in Tables II. and VI. disappear. This seems to be an important result, previously overlooked by experimenters. The advantage of this method over that of filling the air tube alternately with the gas and with air, is that a pure specimen of the gas under investigation is kept in a sealed tube. The difficulty of keeping the air tube, which is more or less open at one end, filled with a pure specimen of such a gas as nitric oxide is obvious. In addition, the waves are produced simultaneously in each tube, so that a difference of frequency is impossible.

Table VIII.

Calculation of results for Nitrous Oxide.

The mean wave-length of 5·483 cm. for nitrous oxide (Table II. tube 1) has now to be multiplied by the factor 6·866/6·849 (Table VII.). The true wave-length then becomes

$$\lambda/2 \text{ air} = 7{\cdot}072 \text{ cm.}$$

$$\lambda/2\ N_2O = 5{\cdot}495 \text{ ,,}$$

Using the physical constants $T_c = 308°{\cdot}5$ abs., $P_c = 75$ atmos., Mol. wt. $= 44{\cdot}02$, for nitrous oxide, and the method of calculation given in the previous paper, the above wave-lengths lead to a value $\kappa = 1{\cdot}302$ at 12°·9 C.

Similarly, the wave-length of 6·453 cm. (Table II. tube 2) is to be increased in the ratio 8·762/8·705, giving the final values

$$\lambda/2 \text{ air} = 8{\cdot}356 \text{ cm.}$$

$$\lambda/2\ N_2O = 6{\cdot}495 \text{ ,,}$$

giving a corresponding value of $\kappa = 1{\cdot}302$ at 11°·6 C.

The final mean results are

whence $\kappa = 1{\cdot}302$, $Cp = 8{\cdot}799$ gm. cals., $Cv = 6{\cdot}758$,, } at 12°·25 C.

TABLE IX.

Calculation of results for Nitric Oxide.

As in the preceding table, the gas tube wave-lengths given in Table VI. require to be multiplied by the factor for their respective tubes. The final wave-lengths then become

Tube 1.	λ air	= 13·382 cm.
	λ NO	= 13·130 „
Tube 2.	$\lambda/2$ air	= 8·594 cm.
	$\lambda/2$ NO	= 8·429 „

The critical data used for nitric oxide are $T_c = 179°{\cdot}5$ abs., $P_c = 71{\cdot}2$ atmos. The molecular weight is 30.

The first set of wave-lengths lead to a value $\kappa = 1{\cdot}401$ at 7°·6 C., and the second to a value $\kappa = 1{\cdot}399$ at 7°·55 C.

The final mean results are then given by

$$\left.\begin{aligned} \kappa &= 1{\cdot}400, \\ Cp &= 6{\cdot}990 \text{ gm. cals.}, \\ Cv &= 4{\cdot}993 \quad \text{„} \end{aligned}\right\} \text{ at } 7°{\cdot}6 \text{ C.}$$

The results for nitrous oxide were also calculated, using Wohl's equation of state*. Values identical with those given above were obtained, and as the equation is more complicated than Berthelot's, it was not further employed.

Summary.

The ratios of the specific heats of nitrous oxide and of nitric oxide have been determined by a method depending on the relative velocities of sound in these gases and in air. The use of dry air, free from carbon dioxide, as a standard, has been shown to be necessary. It has also been proved that it is necessary to eliminate the effect of the tube on the velocity of sound in the gas contained in it. Wohl's equation of state has no advantage over that of Berthelot for the reduction of the results. Employing Berthelot's

* Nernst, 'Theoretical Chemistry,' 8th edit. p. 258.

equation as the basis of calculation, the following results were obtained :—

TABLE X.

	Nitrous Oxide. 12°·2 C.	Nitric Oxide. 7°·6 C.
Cp/Cv	1·302	1·400
Cp	8·799 gm. cals.	6·990 gm. cals.
Cv.....	6·758 ,,	4·993 ,,

In conclusion, the authors wish to express their thanks to the Kent Education Committee for a maintenance grant to one of them (W. G. S.), and to the authorities of East London College for a grant which contributed to defraying the expense of the work. The experiments described were submitted as part of a Thesis for the Degree of M.Sc. in the University of London by W. G. Shilling.

East London College,
University of London.

XLVI. *On the Question of the Number of Radiating Atoms of Various Dimension within Gaseous Hydrogen, studied from the point of view of Bohr's Atom Model.* *By* P. LASAREFF, *Member of the Academy of Sciences of Petrograd, Director of the Physical Institute of Moscow* *.

THE dimension of the hydrogen atom calculated from Rutherford-Bohr's theory is determined by the radius a of an electron moving round the centre as :

$$a = \frac{h^2}{4\pi^2 me^2}\tau^2, \quad \ldots\ldots\ldots \quad (1)$$

h is Planck's constant, m the electron mass, e its charge, and τ any whole number from 1 to ∞, representing the order of the electron's stable orbit. In the case of a single atom, its dimensions are determined by the formula (1), τ is arbitrary. If we have many atoms, subject to mutual shocks, the dimensions of the electron's orbit, as is easy to understand, could not surpass a certain limit, because of the mutual influence of the electrical fields of atoms. In fact, it is experimentally proved that it is possible to observe only spectral lines for which τ varies from 1 to 15, and in that case the dimensions of the electron orbits are :

from $2a = 1{\cdot}1 \,.\, 10^{-8}$ cm. ($\tau = 1$)

to $2a = 247{\cdot}5 \,.\, 10^{-8}$ cm. ($\tau = 15$).

* Communicated by the Author.

Orbits surpassing the last one are impossible because of the reciprocal shocks of the atoms and the mutual influence of the fields. Rarefaction of the gas permits the maximum of the atom's dimension to increase, and, indeed, in star spectra, spectral lines of hydrogen have been found indicating the existence of atoms with an electron orbit of the order 33. It appears of interest to find out the relative number of atoms of gas radiating and possessing electron orbits of different orders.

As is known, Bohr shows that radiation takes place within hydrogen at the moment when one electron displaces itself from one stable orbit of order τ_0, to another stable orbit of order τ_1, while the light-energy radiated at the times of such a movement equals $q = h\nu$, where ν denotes the frequency of oscillation of the radiated line, and q is determined by the formula

$$q = \frac{2\pi^2 me^4}{h^2}\left\{\frac{1}{\tau_1^2} - \frac{1}{t_0^2}\right\}.$$

If the gas contains N atoms, which emit in one time-unit, at the moment of the electron's displacing from orbit τ_0 to orbit τ_1, a radiation with the wave-length λ (frequency of oscillation ν) then the light-energy radiated by the gas in a time-unit will equal

$$\epsilon = q \,.\, \mathrm{N}.$$

As $q = h\nu = \frac{hc}{\lambda}$ where c is lig t-velocity, we have

$$\epsilon = \frac{\mathrm{N}hc}{\lambda} \quad \text{or} \quad \mathrm{N} = \frac{\epsilon\lambda}{hc}.$$

If we call $\mathrm{N}_{\max.}$ and $(\epsilon\lambda)_{\max.}$ the maximum values of N and $\epsilon\lambda$, we have

$$\frac{\mathrm{N}}{\mathrm{N}_{\max.}} = \frac{\epsilon\lambda}{(\epsilon\lambda)_{\max.}}.$$

Thus, knowing the energy of definite spectral lines ϵ_1, ϵ_2, and their corresponding wave-lengths λ_1, λ_2, we are able to find out the relative number of N in parts of maximum value $\mathrm{N}_{\max.}$, and consequently the distribution of radiating atoms. In the present work we have found out the relative quantities of atoms having electrons displacing themselves from the third, fourth, and fifth orbit to the second one, producing radiation of the first three lines of Balmer's series with wave-lengths equalling 656 $\mu\mu$, 486 $\mu\mu$, and 434 $\mu\mu$. For the purpose of finding the energy ϵ of a definite spectral line, the spectrum of hydrogen in Geisler's tube has been spectrophotometrically compared with the intensity of Hefner's lamp, for which the distribution of energy in the spectrum

has been studied by Ångström. Knowing the relative intensity of the line J_0 and the energy corresponding to the radiation of a wave of the same length in Hefner's lamp J_N, we get the relative value of $\epsilon = J_0 . J_H$. Multiplying $J_0 . J_H$ by the corresponding λ we find the relative value N, which, divided by $(J_0 J_H \lambda)_{max.}$, gives a relative value of N (the $N_{max.}$ being accepted as unit).

Heisler's hydrogen tube was excited by a large inductor with an Apex gas interrupter. This interrupted current was chosen of such an intensity that the brightness of the light on the field of König-Marten's spectrometer would be convenient for photometry.

The tube was placed in parallel to the one spectrometer's slit, and with the help of a lens was projected at that one slit; a prism of total reflexion was installed opposite the other slit, sending through that second slit rays of Hefner's lamp.

The results obtained may be found in the Table below, in which τ designates the order of the orbit from which the electron had displaced itself to the second orbit:

TABLE.

λ.	τ.	$\frac{N}{N_{max.}}$.
656	3	1·000
486	4	0·251
434	5	0·175

From all the measures quoted it will be seen that in Heisler's tube, radiating under the influence of an electric discharge and filled with hydrogen, most of the electrons causing the radiation move over from the third orbit to the second. The quantity of electrons springing from the fourth orbit to the second equals only 25 per cent. of that first quantity and, at last, the quantity of electrons springing over from the fifth to the second orbit equals only 17 per cent.

Thus the quantity of springing electrons decreases with the increasing of the distance of electrons from the centre.

It appears of interest to study further members of Balmer's series and also Lyman's series, that result from the displacing of electrons to the first orbit.

The first of those problems is pointed out as one to be experimentally studied at the Physical Institute.

In conclusion I express my gratitude to Ingenieur V. Lasarev for his photometric work and assistance in calculations.

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XLVII. *Positive Rays in simple Gases.*

By J. J. McHenry, *M.Sc. N.U.I.**

THE object of the following experiments was to study the proportion of atomic and molecular positive rays of the simple gases, under varying conditions of pressure, etc., in the discharge tube. It has been pointed out by Sir J. J. Thomson that such a study would probably throw some light on the nature of ionization by cathode rays and the positive rays themselves, and also give some information on dissociation and the forces that bind the atoms in a molecule together.

The apparatus used was essentially the same as that described by Sir J. J. Thomson in 'Rays of Positive Electricity,' p. 57. The Kanalstrahlen were given a horizontal deflexion by means of an electrostatic field and then were deflected vertically on to a parabolic slit by means of a magnetic field. Behind the slit was a Faraday cylinder connected to a quadrant electrometer. The currents registered by the electrometer were proportional to the numbers of positive rays falling on the slit and are given throughout in arbitrary units.

The fast or slow positive rays could be analysed as desired by using a large or small electrostatic field to deflect them on to the slit. In our experiments a field of 40 volts between the plates gave us our slow Kanalstrahlen, while those of higher energy could be brought on to the slit by fields of 80–300 volts. In order to understand this method of working, it is convenient to remember the following facts. The energy possessed by a positive ray is proportional to the voltage E through which it has fallen to the cathode,

$$\text{or} \quad \mathrm{E}e = \tfrac{1}{2}mv^2.$$

Its energy is also proportional to the field required to give it a fixed horizontal deflexion, thus in our experiments, if a voltage V between the plates is required to impart a horizontal deflexion equal to that of the slit, this voltage V is proportional to the energy of the positive ray. In the curves shown, then, and marked 40 volts, 80 volts, etc., the energy possessed by the Kanalstrahlen examined is proportional to the voltage figure shown. Also if a magnetic field H brings the Kanalstrahlen of a given mass on to the slit when the voltage between the plates is V, then from the relation $\mathrm{V}^2/\mathrm{H} = \text{const.}$ we can calculate the magnetic field that would be required with any other voltage.

Finally, when V is fixed if a magnetic field H brings the

* Communicated by Sir J. J. Thomson, O.M., F.R.S.

Kanalstrahlen of mass "m" on to the slit, from the relation H^2/m = constant can be found the field required to bring those of any other mass on to the slit.

In performing the experiment V was kept constant, and a curve plotted showing the deflexion of the electrometer against H the magnetic field, as explained (*loc. cit.* pp. 58–59). The curves we obtained in this way were not very sharp, owing to a slight rotation of the slit, but were sufficiently so to enable us to separate clearly the molecular from the atomic Kanalstrahlen in the simple gases.

In our preliminary experiments with oxygen, the ratio O_1/O_2 was found to be very unsteady—sometimes the atom and sometimes the molecule predominated. It was then found that the presence or absence of mercury in the discharge-tube accounted for the phenomenon. The gas used was stored in a mercury reservoir and then flowed through a capillary tube into the discharge-tube, the pressure being kept low by means of a Gaede mercury pump. The gas was thus always more or less contaminated with mercury vapour.

To test the effect of mercury vapour on the ratio O_1/O_2 the gas was passed over a tube cooled in liquid air in order to remove the mercury vapour.

When the discharge had taken place for some time and the mercury removed by the liquid air-trap, O_1/O_2 was found to be about $\frac{1}{3}$—the molecular positive rays being about three times as numerous as the atomic ones. When mercury was allowed into the tube, by removing the liquid air from the trap, the ratio O_1/O_2 became about 1. This was repeated several times and the molecule could always be brought into great prominence by removing the mercury by cooling.

The following table further illustrates this point. The first two columns give the number of atomic and molecular positive rays in oxygen from which the mercury had been removed by cooling in liquid air. The molecular positive rays are much the more numerous. In the second two columns the mercury was not removed, and here it will be seen that the atom predominates :—

Table I.—Oxygen.

	Without Mercury.		With Mercury.	
	O_1.	O_2.	O_1.	O_2.
V=40.....	245	190		
V=80.....	220	>800	off scale	400
V=120	135	575	>600	250
V=160	35	125	140	80

It will be noticed in the last two columns that the atomic positive rays were more numerous than the molecular, even in those of highest energy, as shown by the last numbers (V=160).

This is important, because in all of our experiments with pure oxygen, the fastest positive rays are mostly molecular, even at very high pressures. The same rule applied to positive rays in hydrogen and nitrogen.

This effect of mercury, of causing the Kanalstrahlen to be mostly atomic, seemed to take place only when oxygen was in the tube. The presence of mercury seemed to have no effect on nitrogen positive rays. In one experiment the nitrogen Kanalstrahlen were analysed when there was no mercury vapour in the tube, the positive column showing the familiar nitrogen pink colour. The experiment was repeated with so much mercury in the tube that the pink colour in the positive column entirely disappeared, and only the greyish colour of the mercury discharge was seen. The curves obtained in the two cases were practically identical, so that the presence of mercury vapour did not seem to affect the nitrogen Kanalstrahlen. Similarly, we found no effect of mercury on the hydrogen Kanalstrahlen. It may be that radiation emitted by the mercury in the tube can cause the dissociation of the oxygen molecules, while not affecting nitrogen or hydrogen. This point will be referred to later.

In order to eliminate mercury from the discharge-tube, we placed a cooling trap on either side of the discharge-tube. One trap prevented mercury or other vapours from entering the tube with the gas stream, while the other trap prevented the diffusion of mercury from the pump into the discharge-tube, the traps being kept in liquid air.

Production of Atomic Positive Rays near the Cathode.

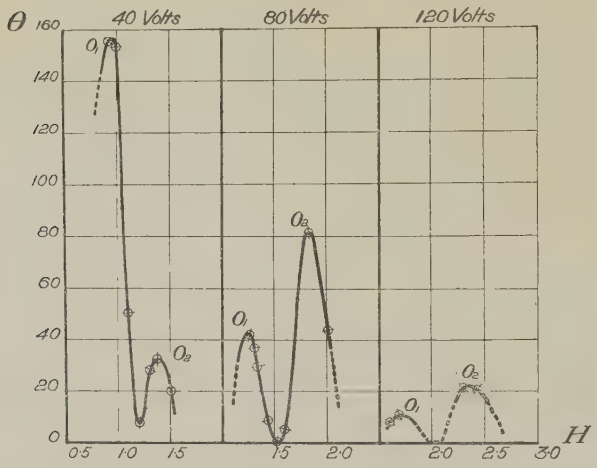
With the gas thus purified a series of experiments was made with oxygen, the Kanalstrahlen of different energies being brought on to the slit as described by different electrostatic fields between the plates. In all the experiments the slower Kanalstrahlen, brought on the slit by 40 volts between the plates, were mostly atomic, while those of greater energy were mostly molecular.

Since the energy of a positive ray depends upon the potential difference through which it falls into the cathode, those of small energy are those produced near the cathode, while those of greater energy are produced at greater distances from the cathode, if we assume that they suffer no loss of energy by collision, etc. The production of atomic

Kanalstrahlen near the cathode is very noticeable at high pressures, but, even at the very highest pressures used, the faster positive rays are mostly molecular. This will be seen in figs. 1, 2, and 3.

In fig. 1 the pressure of the oxygen in the discharge-tube was such that, with a potential of about 5000 volts on the tube (equivalent spark-gap 1 mm.), a current of 2 milliamperes passed through, and the boundary of the dark space was clearly visible, the length of the dark space being about 4 cms. In the 40 volts curve the atomic peak is very striking. The molecule is more numerous in the 80 and

Fig. 1.



120 volt curves than the atom. Fig. 2 is taken with a slightly lower pressure, the current through the tube being about 1 milliampere, and the potential on the tube about 6000 volts. The atomic peak in the 40 volt curve is now depressed and the molecular peaks in the 80 and 120 volt curves are raised. Fig. 3 is taken at lower pressure still, the voltage being about 11,000 and the current little more than ·6 milliamp. The atom is of the same order as the molecule in the 40 volt curve, but in the succeeding curves, 80, 120, and 160 volts (the latter not shown in the figure), the molecular positive rays are about three times as numerous as the atomic.

These general features are reproduced in the analysis of hydrogen and nitrogen positive rays. Curves very similar

to fig. 1 are obtained with hydrogen when the tube is running a good deal harder than with oxygen, the equivalent spark-gap being 4 mm. (14,000 volts) and the current

Fig. 2.

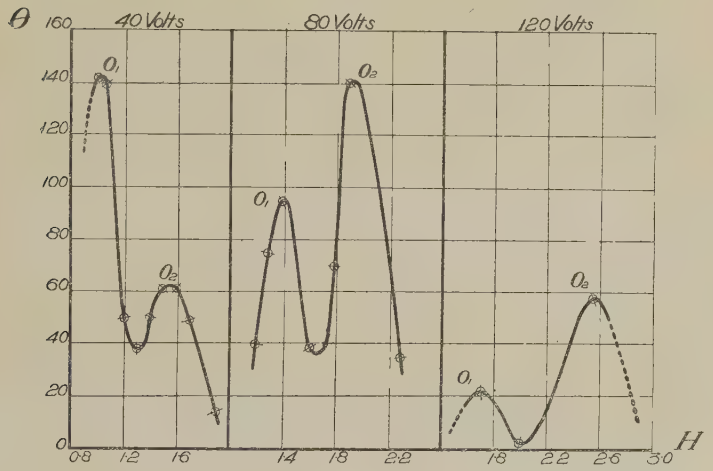
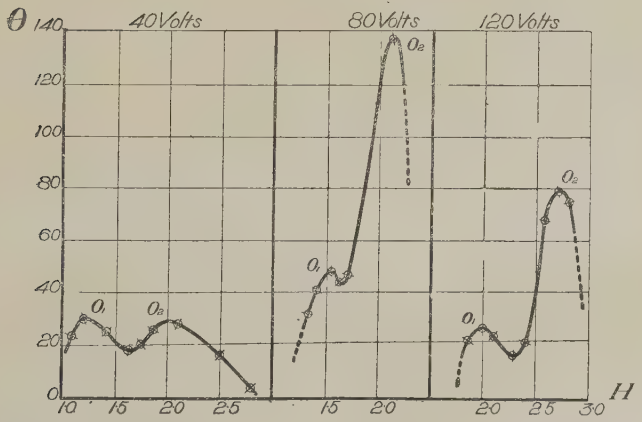


Fig. 3.



through the tube ·3 milliamp. Running the tube harder still the curves become like those shown in fig. 3 for oxygen.

A simple explanation of these results is obtained if we suppose the molecular positive rays to be produced by

cathode rays, while the positive rays themselves when they ionize the gas tend to produce atomic rather than molecular ions. When a primary cathode ray collides with a molecule and ionizes it, the electron knocked off soon acquires sufficient speed under the fall of potential in the dark space to be again able to ionize. Ionization by the cathode rays or electrons increases, then, as we go away from the cathode, so that most of the Kanalstrahlen thus produced fall through the greater part of the potential fall of the dark space, and consequently constitute the faster positive rays. These we have found in our experiments to be mostly molecules.

Ionization by the positive rays, on the other hand, would increase towards the cathode, though it is appreciable all through the dark space, as a positive ray needs to fall through a field of only about 100 volts in order to ionize. The ions produced by the positive rays themselves are then mostly formed near the cathode, and these slow positive rays we found to be mostly atomic.

On this view, then, ionization by cathode rays in general takes place without the dissociation of the molecules, while the more violent nature of the ionization by the positive rays produces charged atoms, one or both of which are positively charged.

The explanation of the results may, however, not be quite so simple. It is pointed out by Dr. Aston (Proc. Camb. Phil. Soc., May 1920) that the energy distribution of the positive rays in hydrogen greatly depends upon the shape of the cathode. When the cathode was convex, so that the cathode rays were not concentrated along the axis of the tube, the results obtained by Dr. Aston were similar to ours—the fast Kanalstrahlen were molecular, the slow ones atomic, the energy of the molecular positive rays being about twice that of the atomic, so that their velocities were the same. These slow atoms are attributed by Dr. Aston to the dissociation behind the cathode of molecular positive rays into two atoms, one positively charged, the other neutral. The primary molecular rays he supposes to be those ions which drift from the negative glow into the dark space, and fall into the cathode under the fall of potential in the dark space.

With concave cathodes, Dr. Aston found that the atomic positive rays were the primary ones, and molecules were formed by the capture of a neutral hydrogen atom. In this case the fast Kanalstrahlen were atomic—the slower ones molecular. As the use of a concave cathode produces a large increase in the intensity of the axial cathode beam, he

attributed the formation of the atomic Kanalstrahlen to the cathode rays.

Further experiments by the electrical method would be required to study these points, using cathodes of different shapes. The cathode used in our experiments combined the convex and concave shapes, being concave close to the centre, and gave a well-pronounced axial beam of cathode rays. It was not altered during the course of the experiments. However the atomic and molecular positive rays are produced, the similar behaviour of oxygen, nitrogen, and hydrogen positive rays found by us shows that the mechanism of ionization and dissociation in discharge-tubes is the same for all three simple gases.

Deflexion of Cathode Rays by Magnet.

In our experiments the cathode was so shaped that it gave rise to a conical beam of cathode rays which struck the glass well of the discharge-tube in a broad circular green patch of about 2 cms. radius. The beam was concentrated at the axis of the cone, showing up as a clear line traversing the dark space when the pressure was high. It is evident that only those positive ions which are produced along the axis of the cathode become positive rays. If a positive ion is produced at a distance from the axis of the tube it falls into the cathode obliquely, and hence does not become a positive ray as it does not pass through the cathode capillary tube.

Now, if a horse-shoe magnet is placed with one pole above and one pole below the cathode, the cathode rays are deflected from the axis. The further we go from the cathode the more the cathode rays are displaced from the axis, while close to the cathode the rays are only slightly deflected. The slow Kanalstrahlen produced by the cathode rays should be only slightly affected, while the faster ones produced further out should be greatly diminished, when the cathode rays are deflected by the magnet.

This experiment was tried with oxygen at moderate pressures. The cathode rays were given such a deflexion that the circular patch of green phosphorescence opposite the cathode moved a distance equal to its own diameter (4 cms.). Readings were taken of the atomic and molecular positive rays when the cathode rays were deflected, and also when they were undisturbed. The results are shown in the following table, the last column giving approximately the

percentage reduction caused by the deflexion of the cathode beam :—

Table II.

	Cathode rays not deflected.	Cathode rays deflected.	Per cent. reduction.
40 volts.			
Oxygen atom, O_1 ...	205	105	48
„ mol., O_2 ...	95	60	36
80 volts, O_1	67	35	53
„ O_2	175	63	65
120 volts, O_1	23	10	56
„ O_2	120	14	92

The table shows that the slowest molecular positive rays are reduced by 36 per cent., those of medium energy by 65 per cent., and the fastest ones by 92 per cent. when the cathode rays are deflected. The molecular positive rays are thus reduced in increasing measure as we go away from the cathode. This is not so marked in the case of the atomic positive rays. It would then seem likely that the molecular Kanalstrahlen are produced by the beam of primary cathode rays. The large reduction in the number of slow atoms is probably due to the reduction of the faster molecules.

With hydrogen in the tube similar results were obtained, as shown in the following table :—

Table III.

	Cathode rays not deflected.	Cathode rays deflected.	Per cent. reduction.
80 volts, H_1 ...	215	86	60
„ H_2 ...	110	80	27
160 volts, H_1...	71	35	51
„ H_2...	95	43	55

The reduction in hydrogen numbers is of the same order as that in oxygen, it cannot therefore be due to any loss by deflexion of the Kanalstrahlen themselves.

Mixtures of Hydrogen and Oxygen.

Some experiments were now performed with mixtures of various proportions of hydrogen and oxygen in the discharge-tube, with a view to finding if the energy distribution of the hydrogen atom and molecule was the same as that of the oxygen atom and molecule. The gases were mixed in the required proportions and allowed to flow into the discharge-tube through a long capillary tube. A remarkable feature of these experiments is that the hydrogen Kanalstrahlen were always few in comparison with the oxygens and not in proportion to the volume of hydrogen in the discharge-tube. This does not agree with Sir J. J. Thomson's results (Phil. Mag., Aug. 1912, p. 247). There may have been more absorption in our experiments, as we worked with higher pressures, though we might expect, owing to the smaller area which the hydrogen molecule presents for collision to a cathode ray or positive ray, that the number of hydrogen ions produced should be smaller than the number of oxygen ions.

The following table shows the number of hydrogen and oxygen Kanalstrahlen in an experiment with two volumes of oxygen and one volume of hydrogen :—

Table IV.

	O_1.	O_2.	H_1.	H_2.
80 volts	456	500	50	54
120 „	230	380	20	45
160 „	23	55	small	small

It will be seen that the hydrogen and oxygen Kanalstrahlen behave similarly, and that the ratio O_1/O_2 is practically the same as that of H_1/H_2, so that the energy distribution of the hydrogens is similar to that of the oxygens.

The experiment was then performed with two volumes of hydrogen to one volume of oxygen, and in this case it will be seen that, while the hydrogen molecular positive rays were more numerous than the atomic ones, the reverse was the case for oxygen, as the following table shows :—

Table V.

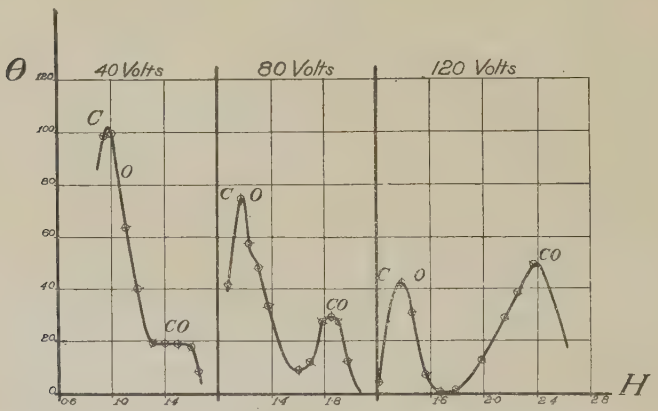
	O_1.	O_2.	H_1.	H_2.
40 volts	200	140	small	($H_1 > H_2$)
80 „	308	184	90	112
120 „	216	220	24	84

The same points will be found in the experiment quoted by Sir J. J. Thomson (Phil. Mag. p. 247 (1912)). In the curves he shows that when the proportion of oxygen was high the molecule predominated, when low the atom came into prominence. Under the conditions of these experiments, however, if (OH) + were formed in large quantities, it would come on the slit for about the same value of magnetic field as the oxygen atom.

Carbon monoxide.

A few experiments were performed with carbon monoxide in the discharge-tube. The proportion of atomic Kanalstrahlen is much greater than with pure oxygen under similar conditions. This will be seen from fig. 4, which

Fig. 4.



shows an analysis of CO. In this experiment the tube was quite hard and the pressure low. The equivalent spark-gap was about 6 mm., showing a potential of about 17,000 volts on the tube. Under similar conditions with oxygen the atomic peaks would be very small, as shown in fig. 3.

An analysis of CO by the electrical method is given by Dr. Aston (Phil. Mag. p. 246 (1912)), and here the molecular peak CO is very high in comparison with the atomic numbers. A field of 320 volts, however, was used by Dr. Aston to bring the particles on the slit, so that his tube was probably harder than ours and the pressure lower.

The ease with which this carbon compound is broken up suggests a possible explanation for the effect which we attributed to mercury of making the oxygen Kanalstrahlen mostly atomic. If the oxygen passing into the tube and coming in contact with tap-grease, etc., brought with it an appreciable quantity of hydrocarbons, or formed CO_2 and CO, these impurities (except CO perhaps) would be removed

with the mercury vapour when passed over liquid air, and would pass into the tube again when the liquid air was removed. The gases CO_2 and CO cause a coloration in the discharge-tube similar to that of mercury, while the presence of mercury is most easily detected spectroscopically.

We tried one experiment where this source of error was eliminated. The usual liquid air-traps were on either side of the discharge-tube, so that the oxygen was free from all vaporous impurities. A side-tube was connected directly to the bulb containing a small pellet of mercury, and this was warmed to make the mercury pass into the discharge-tube. When this was done, however, the tube became rapidly so hard that it was impossible to take any observations, the discharge becoming irregular and finally ceasing. The mercury vapour, perhaps, in being absorbed by the two cooling tubes swept the gas out along with it. This point was not further investigated, as the ease with which CO was broken into atoms had not then been observed.

If this supposition that carbon compounds and not mercury vapour are responsible for the effect we observed in oxygen be correct, it would explain why similar effects were not obtained with nitrogen and hydrogen, as these most inactive gases would not attack the stopper-grease and cause the carbon compounds to come into the tube.

A series of experiments with concave and plane cathodes, using the electrical method to measure the Kanalstrahlen, would give interesting results bearing on the suggestions made in this paper.

The energy distribution of the positive rays is best studied by using quite a short parabolic slit—that used in our later experiments being only about 4 mm. long. The use of this short slit enables the energy distribution to be ascertained sharply, as it prevents overlapping of slow and fast Kanalstrahlen in the measurements. Figs. 1 and 4 were obtained with the short slit. The positive ray current was still big enough to be easily measured by our electrometer, which in our experiments was never used at its highest sensitivity. It would be a great advantage to have the slit cut in a plate separate from the rest of the apparatus, and waxed on, so as to admit of easy alteration both in position and size. Also, instead of an induction-coil with its intermittent discharge, a steady source of high potential would be a great advantage in these experiments.

The above experiments were carried out in the Cavendish Laboratory, Cambridge, at the suggestion of Sir J. J. Thomson, O.M., for whose kind interest and direction throughout the work the author is extremely grateful.

XLVIII. *Ionization by Collision.* *By* J. S. Townsend, *F.R.S., Wykeham Professor of Physics, Oxford* *.

1. SEVERAL suggestions have recently been made with regard to the processes of ionization occurring in discharges through gases, but in many cases they do not appear to have been carefully considered in relation to the principal properties of the phenomena to which they are applied. There are various hypotheses on which some properties of electric currents might be explained; but in order to obtain a satisfactory theory, it is necessary to account for various types of discharge and for the small currents obtained with forces less than those required to produce a disruptive or a glow discharge. In most of the explanations that have been proposed, the ionization has been attributed either to direct or indirect effects of collisions of electrons and positive ions with molecules of the gas or to electrons set free by collisions of positive ions with the negative electrode.

2. In order to test the theory of ionization by collision which I gave many years ago, several sets of experiments had been made on the currents obtained between parallel plates when the initial conductivity was produced either by Rontgen rays or by ultra-violet light. The rate of increase of the current with the distance between the plates was measured for definite electric forces and pressures of the gas, and it was found that the development of the currents was independent of the initial ionization. Thus when ultra-violet light traversed the gas and fell on the negative electrode, the proportion in which the current increased with the distance between the plates was the same with strong light as with light of small intensity. It is therefore clear that the radiation which set free the electrons from the negative electrode did not affect the gas in such a way as to facilitate the genesis of ions by collision. The currents in all these cases were very small, and the number of collisions between electrons or ions with molecules of the gas in the course of an experiment was small compared with the number of molecules in the path of the current. The ratio of the number of collisions to the number of molecules was generally much less than $1 : 10^4$; so that in these experiments two collisions with the same molecule occurred very rarely, and effects that may arise

* Communicated by the Author.

from this cause would be inappreciable. If, for example, a molecule is dissociated by one collision, the number of atoms would be very small compared with the number of molecules in the gas, and the number of electrons generated by collisions with atoms is negligible in comparison with the number generated by collisions with molecules. This is also proved by the fact that the proportion in which the current increases with the distance between the plates is independent of the number of electrons set free initially from the negative electrode. In forming a theory to account for the increase of current with the electric force or with the distance between the plates which is observed in these experiments, it is unnecessary to consider ions which might be formed as a result of two collisions with the same molecule, or by collisions of electrons with molecules that may have been disturbed from their normal state by radiation.

The experiments show that the increase of the currents with the distance between the plates is due principally to ionization of molecules of the gas by the collisions of the electrons, since the number n of electrons arriving at the positive electrode is given by the formula $n = n_0 \epsilon^{ax}$ for a considerable range of distances x between the plates, when the electric force X is constant. With larger distances between the plates the currents increase more rapidly than the value of n as given by this formula, and eventually at a certain distance S a spark discharge is obtained with the potential $S \times X$. Thus it is necessary to assume that another process of ionization is taking place, in addition to the direct effect of the electrons, which does not produce any remarkable effect in the currents obtained with the shorter distances x, but has a large effect as x approaches the sparking distance S.

The additional ionization may apparently be attributed to ionization of molecules of the gas by the collisions of positive ions, or to electrons set free from the negative electrode by impacts of positive ions, or to radiation from molecules of the gas falling on the negative electrode and setting free electrons, this radiation being due to collisions of electrons with the molecules. The question then arose as to which of these modes of producing ions combined with the direct ionization by the collisions of electrons with molecules gives the most satisfactory explanation of the sparking-potentials when the pressure of the gas is above that coresponding to the minimum sparking-potential, and of the small currents obtained with

various distances between the electrodes when ultra-violet light from an external source falls on the negative electrode.

There were several reasons for attributing the additional ionization to the collisions of positive ions with molecules of the gas, and this theory is supported by the results of many recent experiments.

3. Some of the experiments bearing on these points have been made only with simple gases such as nitrogen and hydrogen, but the general conclusions to which they lead probably apply also to monatomic gases. Also, in the experiments on the conductivity between parallel plates and the corona discharges from the surface of a wire to a coaxial cylinder the electrodes have been made of ordinary metals such as copper, zinc, silver, etc., and it is impossible to apply the general conclusions deduced from these experiments to cases where the electrodes are of magnesium or alkali metals. With these metals, large numbers of electrons are set free from the surface by the action of ordinary light, and electric discharges between electrodes of these metals are maintained with comparatively small forces. This is probably due to the action of radiation from the discharge or to the impact of positive ions which cause large numbers of electrons to be set free from the surface of the alkali cathode under conditions where very few electrons would be set free from a cathode of an ordinary metal *.

4. The currents obtained between parallel plates at various distances apart when ultra-violet light falls on the negative electrode may be compared with formulæ for the currents obtained on the hypotheses which have been suggested above. The formulæ † have already been given for the case (A) where α is the average number of molecules of the gas ionized by an electron in moving through a centimetre in the direction of the electric force, and β the number of molecules ionized by positive ions, and the case (B) where a similar action is attributed to the electrons, but the positive ions, instead of ionizing molecules of the gas, are supposed to contribute to the ionization by setting free electrons when they collide with the negative electrode.

The formulæ for the number n of electrons reaching the

* 'Electricity in Gases,' pp. 409, 437.
† 'Electricity in Gases,' pp. 315, 331.

positive electrode under these two conditions are :

$$\text{(A)} \qquad n = n_0 \frac{(\alpha-\beta)\,\epsilon^{(\alpha-\beta)x}}{\alpha-\beta\,\epsilon^{(\alpha-\beta)x}},$$

and

$$\text{(B)} \qquad n = n_0 \frac{\epsilon^{\alpha x}}{1-\gamma(\epsilon^{\alpha x}-1)}.$$

In the second formula the coefficient γ is the ratio of the number of electrons set free by impacts from the cathode to the number of positive ions that impinge on the surface.

In order to obtain a formula for the third case (C), where, in addition to the ionization produced by the collisions of electrons with molecules of the gas, some electrons are supposed to be set free from the cathode by the radiation from molecules of the gas, it is necessary to consider the question of the absorption of the radiation by the gas.

Definite information on this point, and on other points connected with the hypotheses which may be adopted to explain the currents between parallel plates, is obtained from experiments on the currents between a wire and a coaxial cylinder. The force at the surface of a wire required to maintain a glow discharge is connected by a definite relation with the sparking-potentials for parallel-plate electrodes, which shows that the currents obtained in the two cases depend on the same processes of ionization, so that it must be possible to explain both types of discharge by the same hypothesis *. In the case of the radial field of force between a wire and a coaxial cylinder, there is a critical value X_1 of the force at the surface of the wire with which a small continuous glow discharge is maintained between the wire and the cylinder ; and if a be the radius of the wire, and b the radius of the cylinder, the force X_1 is independent of the radius b provided b is greater than a certain radius c. The value of c depends on a and on the pressure of the gas.

In order to account for the fact that X_1 is independent of b, it is necessary to assume in the case of a positive current flowing from the wire to the cylinder either that there are no electrons set free from the surface of the cylinder or that the same number are set free from a cylinder of large diameter as from a cylinder of small diameter. The force at the surface of the cylinder is aX_1/b, and by increasing the radius b the intensity of the electric force near the surface of the cylinder may be reduced so that electrons and positive ions would move with such small velocities in passing through

* 'Electricity in Gases,' p. 369.

the space near the surface of the cylinder that they would not generate ions or excite radiation by colliding with molecules of the gas.

It is impossible, therefore, to obtain a satisfactory explanation of the positive currents from a wire to a coaxial cylinder, or the currents between parallel plate electrodes, on the assumption (B) that electrons set free from the negative electrode by impacts of positive ions form an important contribution to the processes by which the ionization is produced, as it is extremely improbable that the number of electrons thus set free is independent of the velocity with which the positive ions impinge on the electrode.

With regard to the third hypothesis (C), where electrons set free from the negative electrode by radiation from the gas are supposed to constitute an important effect, it would be necessary in this case to assume that the radiation emanating from the gas near the wire where the electrons and positive ions move with high velocities is not absorbed by the gas, as the number of electrons set free from the negative electrode must be the same when the radiation traverses different distances through the gas to cylinders of various diameters.

If it be assumed that the radiation is of this character, a formula for the currents between parallel plates is easily obtained, since nearly all the radiation from the gas falls on the electrodes when the currents traverse a small space near the centre of the field, and the distance between the electrodes is small compared with the diameter of the electrodes. If $\nu\delta$ be the number of electrons set free from the negative electrode due to radiation excited by the collisions of a number ν of electrons in travelling through a distance x in the direction of the electric force, the formula (C) for the number n of electrons arriving at the positive electrode, when ultra-violet light from an external source acts on the negative electrode, is

$$(C) \qquad n = \frac{n_0 \alpha \epsilon^{\alpha x}}{\alpha - \delta(\epsilon^{\alpha x} - 1)}.$$

When suitable values of the quantities α, β, γ, and δ are chosen, the values of n given by the three formulæ (A), (B), and (C) are found to be in good agreement with the small currents obtained between parallel plates at various distances apart when electrons are set free from the negative electrode by ultra-violet light from an external source. Also the sparking distance is found accurately by equating to zero the

denominators of the expressions multiplying the constant n_0. In each case the same value of α is obtained, so that the experiments are decisive in showing that the ionization is principally due to the direct effect of collisions of electrons with molecules of the gas; but it would be impossible to decide from a set of these experiments which of the other modes of generating ions contributes the additional effect required in order to explain the disruptive discharge. When other experiments are considered, it becomes evident that the first hypothesis (A) is the only one of the three which is consistent with the properties of the currents obtained under various conditions.

5. The experiments on the conductivity of a gas between coaxial cylinders show that in the positive discharge from a wire to a coaxial cylinder it is very improbable that electrons set free from the cylinder by the impacts of positive ions contribute appreciably to the ionization, and if this were the determining factor it would be necessary to suppose that the number set free is independent of the velocity with which the positive ions collide with the negative electrode. This point may be tested by considering the values of γ obtained by comparing formula (B) with the currents between parallel plates for a given pressure of the gas when two different forces are used. For air at one millimetre pressure the values of α and γ are 5·25 and ·00268 respectively when the force is 350 volts per centimetre and 6·3 and ·0053 when the force is 437 volts per centimetre. Hence, in order to be in agreement with these experiments, the number of electrons set free from the negative electrode by impacts of positive ions should be doubled when the velocity of the positive ions is increased by increasing the electric force in the proportion 5 : 4. It must therefore be concluded that the second hypothesis cannot afford a satisfactory explanation of these phenomena.

In order to test the third hypothesis, it is necessary to consider the properties of metal surfaces in connexion with the emission of electrons due to incident radiation. The number of electrons emitted by the action of Rontgen rays or by ultra-violet light varies with different metals, and also with the state of the surface. In the case of ultra-violet light, the number of electrons emitted from a bright metal surface may be fifty times as great as the number emitted from the same surface after it has become oxidized. Hence, in the experiments on the development of currents between parallel plates, the factor by which the currents increase with the distance between the plates should vary with the state of the surface if the total ionization depends on the number of

electrons set free from the negative electrode by radiation from molecules of the gas. No such effect was observed in the earlier experiments, where the electrodes were of zinc, and the values of α and δ obtained by comparing those experiments with formula (C) are nearly exactly the same as the values obtained from the experiments with silver electrodes recently made by Ayres*.

Also, the currents between parallel plates of different metals have been measured by Gill † to test whether the factor by which the currents increase with the electric force depends on the sensitiveness of the plates to radiation. It was found that under the action of ultra-violet of constant intensity the number of electrons emitted from one plate was twenty times the number emitted from another, but the factor by which the currents increased with the electric force was the same with both plates. The experiments cannot therefore be explained on the hypothesis that electrons set free from the negative electrode by radiation from molecules of the gas make an appreciable contribution to the conductivity.

Thus the theory in which the principal effects are attributed to ionization of molecules of the gas by impacts of electrons and positive ions is the only one which affords a consistent explanation of the principal properties of the disruptive discharge between parallel plates, the glow discharge from a cylindrical surface, and the development of the smaller currents between parallel plates.

6. An objection to this theory is put forward in an account given in 'Nature' (vol. cx. p. 623, 4th Nov. 1922) of a theory of sparking-potentials communicated to the Academy of Sciences, Paris, by G. Holst and E. Oosterhuis, where it is stated that Holst and Oosterhuis have proved experimentally that the nature of the cathode has an important influence, and that they support the hypothesis that the positive ions do not produce ionization by contact with gas molecules, but by their electrostatic attraction they can liberate them from the cathode. It appears, however, from the account given in the *Comptes Rendus* (vol. clxxv. p. 577, 9th Oct. 1922), that in the experiments made by Holst and Oosterhuis the cathodes were of magnesium or alkali metals, and that their theory is only applied to monatomic gases at pressures near that corresponding to the minimum sparking-potential. It is quite clear that these experiments do not lead to general conclusions with regard to the properties of positive ions.

* T. L. R. Ayres, Phil. Mag. vol. xlv. p. 353 (Feb. 1923).
† E. W. B. Gill, Phil. Mag. vol. xlii. p. 852 (Nov. 1921).

It has been shown by Mey * that the cathode fall of potential in nitrogen, hydrogen, and helium is much less with cathodes of magnesium or alkali metals than with ordinary metals. It is probable that a similar difference due to the electrodes would be found in the minimum sparking-potentials for nitrogen and hydrogen as well as for the monatomic gases, but such a result would not prove that positive ions do not generate ions by collisions with molecules of the gas, or that electrons set free from the cathode by the impact of positive ions make an appreciable contribution to the ionization required to produce a disruptive discharge or a glow discharge from the surface of a wire when the electrodes are of ordinary metals.

7. In the theory of discharges given by Holst and Oosterhuis, the number of molecules ionized by electrons in moving from the negative to the positive electrode is calculated by a method based on unreliable assumptions relating to the conditions under which ions are generated by collisions. When an electron starting from rest moves through the gas under the electric force X, it is assumed that it makes several collisions with molecules in which there is very little loss of energy, and after traversing a certain distance a, it acquires a velocity corresponding to the ionizing potential V_1, and ionizes a molecule of the gas. Thus two electrons start from rest from a plane at a distance a from the cathode, and four at a distance $2a$, the number arriving at the cathode being $2^{(S/a)}$, where S is the distance between the electrodes. The ionizing potential V_1 used in this calculation is the minimum potential under which a stream of electrons acquire sufficient kinetic energy to ionize an appreciable number of molecules of the gas, and it is assumed that the electrons moving through the gas never acquire a velocity greater than that corresponding to the potential V_1. This would only be true if it were probable that a molecule would be ionized in most of the collisions where the velocity of the electron corresponds to V_1. But there is no evidence to show that this is the case as the experiments by which the ionizing potential V_1 is found only indicate that ions are produced in appreciable numbers, which may be very small compared with the total number of collisions with molecules of the gas, when the electrons are moving with the velocity corresponding to V_1. Also electrons lose energy in collisions which cause vibrations in molecules of the gas, as shown by ordinary Geissler tubes, and the experiments that have been

* K. Mey, *Ann. d. Phys.* (4) xi. p. 127 (1903).

made to determine the minimum ionizing potential V_1 indicate that the radiation from the molecules is appreciable when a stream of electrons collide with molecules with a velocity corresponding to a potential V_2 which is less than V_1. If it were assumed that electrons lost all their energy in a large proportion of the collisions with the velocity corresponding to V_2, they would very seldom attain a velocity corresponding to V_1, if they made a large number of collisions with molecules of the gas in moving through the distance a under an electric force X.

In order to obtain ionization by collision it is necessary that the electrons should attain velocities greater than that corresponding to V_2, and there is no reason to suppose that they do not also attain velocities greater than that corresponding to V_1. Thus the method by which Holst and Oosterhuis calculate the number of molecules ionized by electrons moving through a given distance is not very reliable. The best test of the hypothesis, however, is to calculate by this method the total ionization produced by electrons moving through argon in a few particular cases and to compare the results with numbers found experimentally. When a small stream of electrons moves under a uniform force X, this theory implies that all the electrons attain a velocity corresponding to the ionizing potential V_1 at a series of distances from the cathode a, $2a$, $3a$, &c., where they lose all their energy by colliding with molecules, and this phenomenon recurs with perfect regularity for a large number of intervals, each of the same length a. If an electron starts from rest and moves under a constant force X, it loses a small proportion of its energy in the collisions with molecules before attaining the velocity corresponding to V_1, so that the distance a is somewhat greater than V_1/X by an amount depending on the pressure of the gas. With the forces and pressures used in the following examples the distance a is very nearly equal to V_1/X, and it is only necessary to find the difference $(V_1/X - a)$ approximately. Various values have been found for the ionizing potential V_1 in argon from 12 to 15·1 volts, and in this calculation the largest value is taken, as it leads to numbers which come nearest to the results obtained experimentally.

8. If the argon be at 5·2 millimetres pressure and the force 208 volts per centimetre, the distance a is approximately $15{\cdot}1/208 = {\cdot}0725$ centimetre. From the numbers given by the author and Mr. Bailey * in the tables of mean

* J. S. Townsend and V. A. Bailey, Phil. Mag. vol. liv. p. 1033, Nov. 1922).

free paths and velocities of electrons in argon it will be found that in passing through this distance in the direction of the electric force, an electron makes on an average about 1300 collisions, in each of which it loses a proportion of its energy equivalent to about one part in 40,000.

The total loss of energy in traversing the distance a is therefore about 3 per cent. of the final energy, so that in order to attain the velocity corresponding to 15·1 volts the electron must traverse a distance ·075 centimetre in the direction of the electric force. In order to make allowance for possible errors it may be supposed that the distance a is ·08 centimetre. Hence the current would be increased by the factor $2^8=256$, if the distance between the plates were increased by ·65 centimetre.

The currents obtained in argon between parallel plates of silver when ultra-violet light acts on the negative electrode have recently been determined by Ayres *, the gas having been purified very carefully. With the gas at 5·2 millimetres pressure, and a force of 208 volts per centimetre, it was found that the increase of current due to collision of electrons with molecules is given by the formula $n=n_0\epsilon^{\alpha x}$, where $\alpha=5{\cdot}05$. Thus the current increases by the factor $\epsilon^{3{\cdot}28}=26{\cdot}5$, when the distance between the plates is increased by ·65 centimetre.

The number obtained by the theory is therefore much too large, and instead of ionization taking place regularly at distances of ·075 or ·08 centimetre, it appears that on an average ionization occurs after the electron travels a distance of ·137 centimetre, ($\cdot137\times5{\cdot}05=\log_e 2$).

9. The preceding experiment where the gas was at 5·2 millimetres pressure is taken as an example, in order that there should be a large number of collisions with molecules when the electrons attain the velocity corresponding to V_1, but when the ratio X/p is of the order 40, small quantities of impurities have a large effect on the value of α, and it might be suggested that the discrepancy between the theory and the experiments is due to this cause. With the larger values of the ratio X/p the effect of impurities is very much less, and it is comparatively easy to avoid errors due to impurities, so that the following experiment may be considered.

In argon at 1·325 millimetre pressure the value of α was found to be 5·76 when the electric force is 252 volts per centimetre, so that the current increases by the factor $\epsilon^{2{\cdot}88}=17{\cdot}8$ when the distance between the plates is increased

* T. L. R. Ayres, *loc. cit.*

by half a centimetre. In this case the distance a is approximately ·06 centimetre, and an increase of half a centimetre in the distance between the plates would, according to the theory, increase the current by the factor $2^8 = 256$, which differs from the number obtained experimentally to a greater extent than in the example where the gas was at 5·2 millimetres pressure.

If the values of α which have been obtained for helium be considered it will be found that the value of the ionizing potential usually given is too high. Experiments are being made on this point which will be described in a future communication.

10. There are many simple experiments which show that all the electrons do not acquire maximum and minimum velocities at the same regular intervals from the cathode, when a small current flows through a gas under a uniform electric force. Thus the experiments on the determination of the quality α, and the experiments on the motion of electrons in gases, show that the velocity of agitation and the velocity in the direction of the electric force becomes independent of the distance from the cathode after the stream has traversed a short distance through the gas, under a uniform electric force.

A distribution of the velocities where various effects due to impacts recur at regular intervals, occurs in the case of the striated positive column in a discharge-tube, but this phenomenon is only observed when the current is comparatively large and the electric force attains a maximum and minimum value in each striation, due to the charge in the gas.

11. The question arises as to what extent the mean loss of energy of electrons in collisions with molecules is affected when the velocity of the electrons is increased from below the critical value corresponding to the potential V_2 to a velocity above this value.

Several experiments have been made to determine the critical potentials required to produce various effects in gases, and in order to compare the results with other investigations, some of the values that have been obtained for argon and hydrogen may be considered. Prof. Horton and Miss Davies* have deduced from their experiments with argon, that the minimum ionizing potential V_1 is 15·1 volts, and the minimum potential V_2 required to excite radiation is 11·5 volts, and that ionization or radiation does not always occur when electrons collide with molecules with velocities corresponding to these potentials, but the proportion of the total number of

* F. Horton and Miss A. C. Davies, Proc. Roy. Soc. A. vol. xcvii. pp. 1, 27 (1920).

collisions with the larger velocity in which ionization takes place is increased when radiation is excited by a large number of collisions with the smaller velocity.

In these experiments the electrons that collide with the molecules are emitted by a hot filament, and the emission current may be of the order of a milliampere. A large proportion of the molecules in the path of the stream of electrons emitted by the filament may therefore receive several impacts per second from electrons moving with velocities greater than that corresponding to the potential V_2, and it is possible that the ionization which is attributed to collisions with the velocity corresponding to V_1 is principally due to the ionization of molecules which had been affected by previous collisions. As the intensity of the stream of electrons from the filament is not stated in the published account of these researches, it is not possible to estimate the probability of ions being generated when an electron collides with a molecule in its normal state.

These experiments therefore do not show definitely that an appreciable number of molecules are ionized by collisions where the velocity of the electrons corresponds to 15·1 volts when a small current is passing through the gas, as in cases where the stream of electrons is measured by an electrometer, and it is impossible to estimate, from the value obtained for V_1, the number of ions generated per centimetre by an electron moving through a gas under a constant electric force.

Some information as to the probability of electrons losing all their kinetic energy in collisions with the velocity corresponding to V_2 may be obtained from the experiments on the motion of electrons in gases. In argon when a stream of electrons moves through the gas at 20 millimetres pressure under a force of 25 volts per centimetre, the mean energy of agitation attains a value corresponding to 12 volts, and the ratio of the mean loss of energy of an electron in a collision with a molecule to the mean energy of agitation is $3{\cdot}5 \times 10^{-5}$. Thus the proportion of collisions with velocity corresponding to 11·5 volts in which electrons lose all their energy is less than one in 10^4. These experiments on the velocities of electrons in argon lead to the conclusion that, in general, electrons do not lose the greater part of their energy in collisions with normal molecules with velocities less than that corresponding to a potential of about 17 volts.

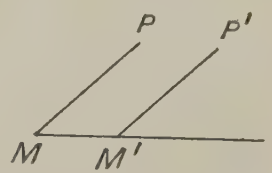
The value of the minimum potential V_1 required to ionize a molecule of hydrogen, V_2 to excite radiation in a molecule, and V_3 to dissociate a molecule given by F. Horton and Miss A. C. Davies, are $V_1 = 16{\cdot}9$ volts, $V_2 = 13{\cdot}9$ volts, and

$V_3 = 2{\cdot}5$ volts. When a stream of electrons moves through hydrogen under a constant electric force X_0, and each electron makes several collisions with molecules of the gas in passing through a distance of the order V_1/X, the number of ions generated by collisions would be extremely small if the electrons lost the greater part of their energy in collisions with velocities greater than 2·5 volts. The experiments that have been made on the motion of electrons in hydrogen show that the ratio λ of the mean loss of energy of electrons in collisions with molecules, to the mean energy of agitation of the electrons, increases continuously with the velocity of agitation, the values of λ being $4\,5 \times 10^{-3}$, 9×10^{-3}, and 25×10^{-3} for the velocities of agitation corresponding to one volt, 2 5 volts, and 4 volts respectively. Thus when collisions occur with velocities considerably greater than that corresponding to 2·5 volts, the average loss of energy is a small fraction of the kinetic energy of the electron. These experiments show that if molecules of hydrogen are dissociated by electrons moving with a velocity corresponding to 2·5 volts, it is only in a small proportion of the total number of collisions that dissociation occurs.

XLIX. *Suggestions regarding an Alternative Theory.* *By* C. H. Bickerdike *.

ACCORDING to the classical conception of Faraday lines, the existence of matter affects the state of the æther in some degree, however small, at any distance from the matter. In that respect there is an important difference between the relation of matter to the æther and the relation of a body floating in water to the water.

When matter is in uniform motion, the Faraday lines are carried along with it—*i. e.*, the state of the æther at any point at any distance from the matter is being altered. If the matter is at one moment at the point M, the æther is in a certain state at a point P. When the matter has arrived at M′, the state of the æther which was formerly found at P is now found at P′. In Relativity theory the same idea is expressed by saying that matter affects the state of "space" and this state moves as the matter moves. It



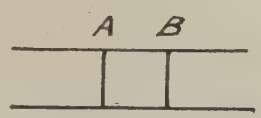
* Communicated by the Author.

is very important to remember, however, that the essential point about the Faraday line conception is that the state of the æther is differentiated particularly along the direction MP. It is not merely that there is, around P, in all directions equally, some difference of state in the æther due to the existence of the matter at M. There is some special significance in the linear direction PM.

The writer prefers to speak of æther rather than of space, since it is admitted that Einstein's "space" is not mere emptiness, but something having properties and capable of being the vehicle of forces. The æther may not be exactly "matter," but it is something which has relations to matter and can interchange energy with matter.

The theory that the existence and the motion of matter imply effects upon the state of the æther at all points distant from the matter has an important bearing on the theory of propagation of wave-motions.

If a sound-wave is started from a vessel floating in or immersed in water, there is no reason for supposing that the state of the water at a distance from the vessel is affected by the existence of the vessel or by its uniform motion in any manner which has a bearing on the velocity of propagation of sound. The principle that the velocity of the sound-wave depends only on certain properties of the medium can be established by imagining the medium to be contained in a tube and taking cross-sections at A and B. The tube is imagined to move with a velocity in the direction opposite to that of the waves, so that the same phase of the wave is always found at A, say a crest or maximum compression, and at B always a hollow or maximum of rarefaction. The supposition is that the state of the medium at A and at B remains constant; and on that supposition it is demonstrated that the velocity $u = \sqrt{\frac{E}{\rho}}$ and is independent of the length of the waves and of the strength of the impulse which started them.

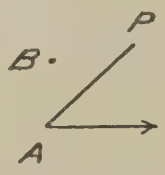


If we now consider the case of waves in the æther—it is immaterial to the point in question that they are transverse, and not longitudinal—propagated from a body which itself has a velocity v, then in order to get the same conditions, that the states of the æther at A and B are constant, we should have to attribute a velocity of $v+c$

to the tube if we are regarding the matter from the point of view of an observer who was not sharing in the motion.

It does not follow that there would be any means of measuring that velocity from an outside point of view. Perhaps all that we are entitled to infer is that the velocity of light should appear constant from point to point on the moving system, to observers on that system.

If light is being emitted by two bodies, A and B, and A has a velocity V in the direction of the arrow, and B is stationary, and if we consider any point P distant from both of them, the Faraday line conception would lead to the conclusion that light travelling along the direction AP from A would have velocity C plus the motion of the line AP, but light travelling along BP need not be affected in anything like the same degree by the fact that the state of the æther along the line AP is in motion. We should expect only that the facts that the matter A exists and that it is in motion, by making the state of the æther at P not quite identical with what it would otherwise be, would have some kind of effect upon radiation emitted by B and passing through P. The existence of A implies a gravitational field, and it is not unreasonable to suppose that this is intimately related to the Faraday lines. The bending of light on passing through a gravitational field may be the effect caused by the mere existence of A and its lines on the light travelling along the direction BP. There may be also a further effect if the gravitational field and the lines are in motion.



The connexion between Faraday lines and gravitation, and the apparent similarity of gravitational attractions and centrifugal forces due to rotation, will be referred to again later. Something has to be said first, however, on the question whether the theory suggested is in accordance with observed facts, such as Majorana's experiments. The question of Aberration is dealt with later.

The Michelson-Morley Experiment and the Lorentz Transformation.

On the supposition that light is transmitted at constant velocity through a stationary æther, the distance traversed by the light at right angles to the earth's motion is $\frac{2l}{1-\frac{v^2}{c^2}}$,

and that traversed by the light in the direction of the earth's motion is $\frac{2l}{\sqrt{1-\frac{v^2}{c^2}}}$, v being the velocity of the earth.

On the theory which the writer suggests, the two distances would both be equal to $2l$ measured along the earth's lines, because the Faraday lines belonging to the earth partake of its motion, and the light travels along those lines with a velocity constant relative to them. But if one take the standpoint of a spectator on the sun, the velocity of the light along the direction of motion of the earth is $v+c$ one way and $v-c$ the other way.

That is not to say, however, that the spectator stationary relative to the sun would have any easy way of measuring these velocities. We cannot measure the velocity of light in a direct manner analogous to the measurement of the velocity of sound.

The Lorentz transformation is obtained by assuming that the velocity of light must be made to be constant, and equal to c only, in each direction. That necessitates that the length along the direction of motion must be regarded, from the point of view of an observer not sharing in the motion, as contracted, and that a corresponding change in the measurement of time is made. This only means, however, that the results, so far as regards observations made entirely from the origin of axes, are *as if* the lengths were contracted and the times varied in accordance with the formulæ.

The actually observed results of measurement of the velocity of light are, as a matter of fact, too inexact to furnish any certain conclusion that the velocity is constant as measured when the light is reflected back to the one observer. Assuming, however, that this constancy is observed, it can be accounted for on the theory above suggested; and the Lorentz transformations are then to be regarded as merely fictitious devices for expressing the truth in a way which may have some conveniences, but without meaning that the lengths of material bodies and the motions of clocks are, in any real sense, varied in accordance with the transformation of x and x' and of t and t'.

If we consider Einstein's train and the platform, so long as an observer on either of these confines his experiment to light produced on his own system and reflected from mirrors or passed through lenses all on his own system, it may be

believed that he will find the velocity of light constant even if the measurement is made by two observers at a distance from one another. The Faraday line theory would account for that. It is not so obvious, however, what we should suppose would be the case on relativity principles if the light were reflected from one system to the other.

Suppose we have an observer S at the rear end of the platform and another S′ at the rear end of the train, and each produces a flash of light at the moment when the observers are adjacent to one another.

Taking the observer S, on the platform, he is supposed to "judge" that the front end of the train only reaches to a point P on the platform. He has at P a mirror which reflects part of the beam back to S. Another part is reflected across to the train (a very short distance). At the moment when the light reaches P, a part of the train not quite at the front end will be opposite P, say P′, where there is a mirror which reflects the light back to S. Another part of the beam from S goes direct to P′ and is reflected back to S.

Would a toothed-wheel arrangement at S show all these three beams as having the same velocity as judged by S?

We certainly do not know experimentally that this would be the case. Possibly a test might be made by a toothed wheel (or two such wheels adjacent and revolving in opposite directions), the light being reflected back from a great distance in two beams, one from a fixed mirror and one from one of Majorana's rapidly revolving mirrors adjacent to the fixed mirror.

Even so, however, it might be the case that mere transmission through the air would involve loss of any velocity imparted by the revolving mirror.

Indirect inferences from interference are of doubtful import, as may be seen from the following observations on Majorana's experiments.

Majorana's Experiments.

Majorana's well-known experiment, designed to test whether a ballistic theory of the propagation of light is tenable, is described in the Phil. Mag. 1918, pp. 163–174.

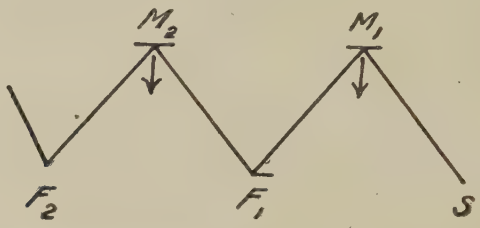
It may be decisive against a simple emission theory which regards light as a stream of projectiles which, on reflexion from mirrors, behave like elastic particles rebounding. It is submitted, however, that the conclusion that the velocity of light is always constant relative to the observer does not necessarily follow. There is an alternative conception which would equally well fit in with the results of the experiment: namely, that the light is propagated along the Faraday lines which belong to and are at rest relatively to the body from which the light proceeds, including the case of reflexion from a mirror, and that the velocity of propagation is constant relative to those lines which themselves have the translatory motion, if any, of the body to which they belong. Relative to the observer, the velocity of propagation would, on this theory, not be equal to c, relatively to a stationary observer, when the light was reflected from a moving mirror; it would be reflected with a velocity $c \pm v$ (according as the mirror was moving towards or away from the observer). In this respect the theory resembles the ballistic theory, but the important difference between the two occurs when that light is again reflected from a fixed mirror. On the ballistic theory, the light reaching the fixed mirror with velocity $c+v$ would be reflected with this velocity and the wave-length would not be altered. On the Faraday line theory, however, the light, though arriving at the stationary mirror with velocity $c+v$, would leave it with velocity c, and the wave-length would necessarily be reduced. On the other hand, if it arrived with velocity $c-v$, and left with velocity c, the wave-length would be increased.

In Majorana's experiment the wave-length would be reduced at each reflexion from the *fixed* mirrors when the moving mirrors were moving towards the source of light, and the reduction would be additive for each such reflexion. The result would be exactly the same as on Majorana's own theory, only the points at which contractions of wave-length would occur would be at the fixed instead of the moving mirrors.

Similarly, on the reversal of the motion, there would be increases of wave-length at each reflexion from the fixed mirrors.

Another possible view is that the light might be supposed to travel along the Faraday lines belonging to the body *on to* which the light was falling. This would operate in substantially the same way as on the previous supposition.

Let S be the source of light, M_1 and M_2 mirrors moving in the direction indicated by the arrows with velocity v resolved along the direction of the lines M_1S, M_1F_1, and M_2F_2. F_1 and F_2 are fixed mirrors.



1. First suppose transmission along the lines *from* which the light is proceeding. The line SM_1 is then stationary. The wave-length is λ, as judged by a stationary observer if he were able to observe it, and the velocity of transmssion along SM_1 is c. Owing to the motion of M_1, there would be, *for an observer on* M_1, a Doppler effect, apparently contracting the wave-length, but the light would be reflected along the line M_1F_1, which would have velocity v, and the light would have velocity $c+v$ towards F_1. The wave-length would still be λ along M_1F_1. The light is then reflected along F_1M_2 with velocity c, and the wave-length is reduced to λ' and is still λ' on reflexion along M_2F_2, and is again reduced further on reflexion from F_2.

In this diagram the mirrors are represented, for simplicity, as all parallel to one another, and the angle of incidence is uniformly the same at each mirror. It is not a picture of Majorana's apparatus.

2. Suppose transmission is along the lines belonging to the system *on to* which the light falls.

The wave-length along the line SM_1, which is moving towards S with velocity v, will now be λ', and the light will travel, relatively to S with velocity $c-v$. It will be reflected along M_1F_1 with velocity c, but the wave-length will not be increased, because the number of waves falling on M_1 per unit of time will be the number emitted by S, say N. That number will be transmitted along M_1F_1 with velocity c, but they will be crowded in just the same way as along SM_1. A further crowding will occur along F_1M_2.

The result of the second experiment appears also to be in accordance with either of these theories. The light, before reaching the eye, is reflected from a stationary mirror. On

the supposition that it is carried along the Faraday lines of the moving source, the wave-length is not reduced by the motion; but on being reflected from the stationary mirror, along the lines of that mirror, the velocity would be c only and there would be a reduction of wave-length. The net result, on reaching the eye, would be the same as if transmission had been all the time through a stationary æther.

On the supposition that transmission is along the lines of the recipient body, the reduction of wave-length would occur at the point of emission, and the result would also be the same as in the case of transmission through a stationary æther.

The discussion in terms of Faraday lines does not, of course, give us any simple physical picture of the æther and of what is happening in it. The æther remains as mysterious as ever, but, it is submitted, not more mysterious than Einstein's "space."

L. *A Determination of the Coefficient of Reflexion of X-Rays for Calcite and Rock-Salt.* *By* Bergen Davis, *Professor of Physics, Columbia University, New York, and* H. M. Terrill *.

WHEN a beam of X-rays, after reflexion from a crystal surface, falls on a second crystal, maximum reflexion is obtained when the planes of the two crystals are parallel. Nevertheless, some reflexion is observed when the second crystal is rocked through a small angle each side of the position of parallelism. This indicates that when a beam of non-homogeneous X-rays falls on a single crystal, not only is there reflexion of the rays of wave-length λ, corresponding to $\lambda = 2d \sin \theta$, but some energy of neighbouring wave-lengths is also reflected. The amount of associated reflexion, as indicated by the width of the rocking curves, depends on the nature of the crystal, the perfection of its crystalline structure, and the condition of the surface. This fact introduces some difficulties in specifying the reflectivity of a crystal.

W. L. Bragg † has defined a quantity which he calls the coefficient of reflexion, and he has determined the value of this coefficient for rock-salt. A similar quantity has been defined by A. H. Compton ‡, and determined for rock-salt and also for calcite.

* Communicated by the Authors.

† Phil. Mag. Jan. 1921 and July 1921.

‡ Phys. Rev. July 1917.

In both cases the expression taken as the coefficient of reflexion is $R=\frac{E\omega}{I_0}$, where E is the total deflexion of the electrometer as the crystal is rotated with an angular velocity ω through an angle covering the wave-length in question, and I_0 the deflexion when the direct beam is allowed to enter the ionization chamber for one second. This expresses the coefficient of reflexion in terms of angle, Compton giving it per degree and Bragg per radian.

It is understood that the beam of X-rays used is in all cases monochromatic, being either a prominent characteristic line of the target used, or a narrow range selected from the general radiation by previous reflexion on another crystal.

Bragg states, as justification for his definition of the coefficient of reflexion, that this quantity makes allowance for the imperfection of the crystal and gives an integrated or average result that will depend on the nature of the crystal and not on its state of perfection.

It is one of the purposes of this paper to show that the coefficient of reflexion is not independent of the crystal surface, but depends greatly on the perfection of this surface.

Investigations of the reflectivity of calcite and rock-salt have been recently completed by Bergen Davis and W. M. Stempel *, using a specially constructed double spectrometer. In these investigations the general radiation passing through the slits fell on the first crystal designated as crystal A. The reflected radiation from this crystal then fell on a second crystal designated as B, and the radiation reflected from B was measured by an ionization chamber in the usual manner.

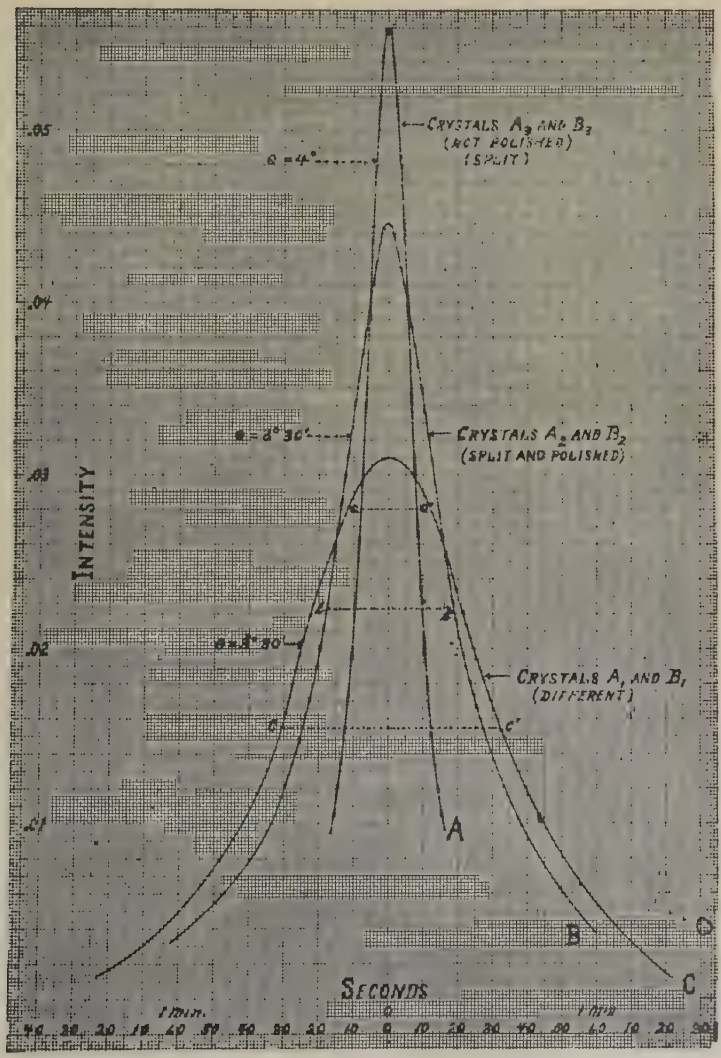
Maximum reflexion was obtained when the crystal planes were parallel, and the curves of intensity called rocking curves were obtained when crystal B was turned on each side of the position of parallelism (see fig. 1). Crystal B was so arranged that it could be moved aside and the beam from A allowed to enter the ionization chamber directly. The ratio of the two intensities, that reflected from *B* at parallelism over that reflected from A, was expressed in percent and called the percent reflexion. This was taken as a measure of the reflectivity of the crystal.

The results of Davis and Stempel can be expressed in terms of the coefficient of reflexion as defined by Bragg

* Phys. Rev. May 1921 and May 1922.

and Compton, and a direct comparison can be made. Each determination of Davis and Stempel consists of a rocking

Fig. 1.—Rocking curves for Calcite.



curve, *i. e.* a curve of intensities at angles close to that of parallelism, and an observation of the intensity of the beam reflected directly from the first crystal. In practice,

the intensities were measured by recording the time required for a unit electrometer deflexion, but the quantities plotted were the reciprocals of these times, giving the deflexions produced in one second.

A rocking curve then is a curve whose abscissæ are angles and whose ordinates electrometer deflexions, or, what is the same thing, intensities. To obtain the coefficient of reflexion from the rocking curve, suppose the axis of abscissæ divided into equal intervals $\Delta\theta$, and that the unit of angular magnitude selected (in this case, one degree) contains m such intervals. Further, draw an ordinate of the curve at the centre of each division, and call the sum of all these ordinates ΣI.

Then, if $\Delta\theta$ is small, the expression $\Sigma I\,\Delta\theta$ will give the area under the curve. But ΣI corresponds to the total deflexion of the electrometer if the crystal had been rotated with an angular velocity $\frac{1}{m}$, since ΣI is the sum of electrometer deflexions and $\frac{1}{m}$ gives the number of degrees passed over per second; whence $\Sigma I \cdot \frac{1}{m} = E\omega$.

We have then

$$\frac{E\omega}{I_0} = \frac{\Sigma I \cdot \frac{1}{m}}{I_0} = \frac{\Sigma I\,\Delta\theta}{I_0 m\,\Delta\theta}.$$

Now the fraction on the right is readily obtained from the rocking curves of Davis and Stempel, by dividing the area under the rocking curve by the area of a rectangle whose height is the intensity of the direct beam and whose length is the angular unit, one degree, on the scale to which the curve is drawn.

Hence, to obtain the coefficient of reflexion as defined by Bragg, it is only necessary to measure the area under the curve with a planimeter and perform the division indicated.

In the case of calcite, observations were made with three pairs of crystals. The first pair is designated as A_1–B_1. A_1 was a specimen of Montana calcite, having slight flaws in the interior and a polished surface. B_1 was an old clear specimen of Iceland spar with its surface polished.

For the second pair, A_2–B_2, a crystal of clear Iceland spar was split, the surfaces polished, and the crystal mounted so that the reflecting surfaces were planes that had been in contact before splitting. The third pair, A_3–B_3, was also obtained by splitting a clear crystal of Iceland spar. The

freshly split surfaces were not polished, and all contact with them was carefully avoided during the process of mounting. As mounted, the two reflecting surfaces were the contiguous planes before splitting.

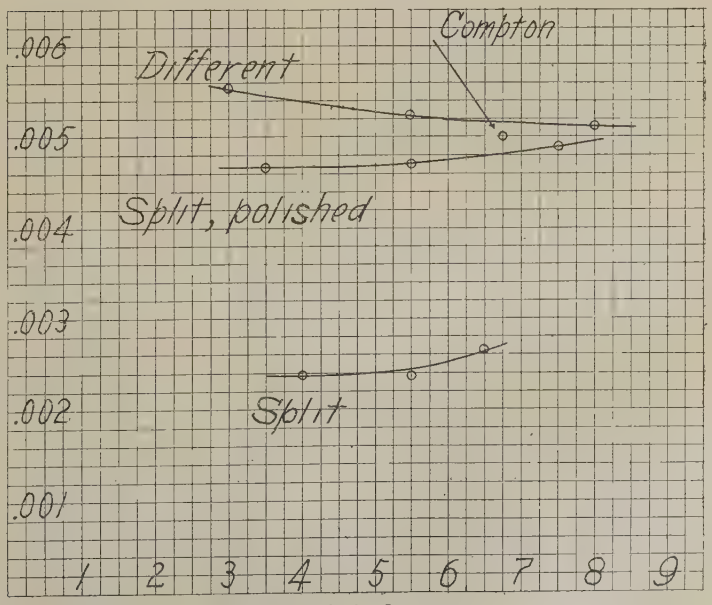
The three pairs showed marked differences in reflectivity and width of the rocking curves. The results obtained are given in the following table and are also exhibited in the curves (fig. 2).

Calcite.

Crystals.	Glancing Angle.	Percent Reflexion.	Coefficient of Reflexion per degree.
$A_1 - B_1$	3° 0′	25·8	·00552
	5° 30′	20·8	·00523
	8° 0′	17·3	·00512
$A_2 - B_2$	3° 30′	35·4	·00466
	5° 30′	29·2	·00470
	7° 30′	25·3	·00489
$A_3 - B_3$	4° 0′	44·4	·00238
	5° 30′	43·1	·00238
	6° 30′	42·8	·00265
Compton	6° 45′	.....	·0050

Fig. 2.

Coefficient of reflexion for Calcite for different glancing angles



Coefficient of reflexion.

Glancing angle in degrees.

The value of the coefficient for the dissimilar polished crystals, A_1–B_1, agrees with that obtained by Compton.

It will be observed that the coefficient obtained for the more perfect pair, A_2–B_2, is about one-half of that obtained for the pair A_3-B_3. Both these pairs were split crystals, the only difference being that the surfaces of the pair A_2–B_2 were polished. Evidently the act of polishing has doubled the coefficient of reflexion.

The table further shows that the coefficient decreases with increasing wave-length for the pair of dissimilar crystals, but that it increases slightly for the two more perfect pairs. Fig. 1 is reproduced from the original paper, and shows rocking curves for the three different pairs of crystals. Attention is called to the extreme narrowness of these curves, in particular for the case of crystals A_3–B_3.

A similar investigation of the reflectivity of rock-salt has been also made by Davis and Stempel. Two sets of rock-salt crystals were employed. They were split and mounted in the same manner as the calcite. Experiments were made both with freshly split surfaces and with polished surfaces, but it was found that polishing did not have a marked effect on the reflectivity.

The rocking curves obtained were somewhat irregular and quite wide, being more than fifty times as wide as the narrowest curves obtained with calcite. However, the curves obtained were not as wide as that found by Bragg for an unpolished crystal.

The curves were integrated, and the coefficient of reflexion is given in the following table :—

Rock-Salt.

Crystals.	Glancing angle.	Percent reflexion.	Coefficient of Reflexion per degree.
Split	3°	24·8	·0480
	5°	15·3	·0294
	7°	13·0	·0214
Washed and polished	3°	22·1	·0462
	5°	15·1	·0309
	7°	11·5	·0231
Compton	7° 15′	.....	·023
Bragg	6° 15′	.....	·031

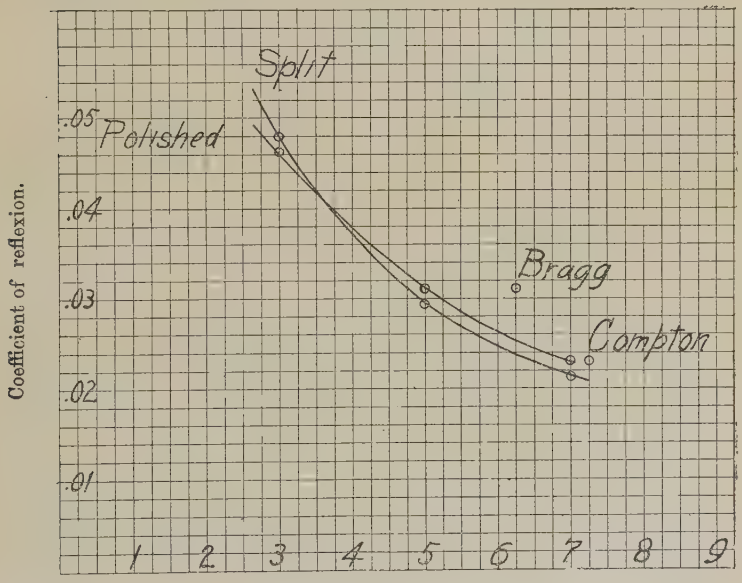
The value listed for Bragg is his final value, taken from the Phil. Mag. July 1921, p. 7, and the angular units changed from radians to degrees by multiplication by 57·3.

The comparison with the values of Bragg and Compton is also exhibited graphically in fig. 3.

The results indicate that the crystal used by Compton was of about the same quality as those of Davis and Stempel, while that of Bragg had a much poorer surface, as evidenced by the higher coefficient obtained and also independently by the wider rocking curve. It is interesting to note that the coefficient of reflexion increases sharply with decreasing

Fig. 3.

Coefficient of reflexion for Rock-Salt for different glancing angles.



wave-length. It would seem that an increase in this direction is characteristic only of crystals of imperfect surfaces, since we find a decrease for perfect calcite, a slight increase for the imperfect calcite, and a sharp increase for rock-salt, which is always far more imperfect than calcite.

In general, a comparison of the reflectivities of rock-salt and calcite cannot be made directly. Rock-salt has a low, wide rocking curve, whose large area gives a high coefficient of reflexion, while the curve for calcite is high and narrow, having smaller area but greater percentage intensity at the

maximum. To say which substance is the better reflector depends entirely on the point of view. Furthermore, in both cases the reflectivity is dependent on the perfection of the crystal surface, a rough surface increasing the width and area of the rocking curve but diminishing its height.

We seem driven to the conclusion that there is no single quantity which can be properly used as a measure of the reflectivity, and that to completely specify the reflecting power of a substance requires the determination of two constants.

One of these might well be the coefficient of reflexion as used by Bragg. Since this involves both the area and height of the rocking curve, the selection of the second quantity becomes rather difficult, if it is desired to have the pair simply related to the fundamental constants of the curve. As simple a selection as any is to take as one of the two required quantities the width of the rocking curve, either at half maximum, or at the points of inflexion, and as the other, the ratio of the reflected to the incident intensities, or the percentage reflexion.

Phœnix Physical Laboratories,
Columbia University.

Note added Nov. 20, 1922.

Since the above was written, there has come to our attention an article by Wagner and Kulenkampff* giving values of the coefficient of reflexion for calcite and rock-salt for longer wave-lengths.

They find for calcite ·0046 per degree at 1·54 and 1·75 Å. Assuming the coefficient for calcite to be approximately independent of the wave-length, we take this value to indicate that the crystal used was of about the same degree of perfection as our A_2–B_2.

For rock-salt they obtain ·0157 per degree at 1·54 Å and ·0145 at 1·95 Å. These values show that the decrease in the coefficient with increasing wave-length that we observed for short wave-lengths still holds at the longer wave-lengths.

Incidentally they mention a remark of Küstner † that in the original observations of Davis and Stempel the voltage employed was so high as to cause overlapping of the second order at the longer wave-lengths. This is an error ; the voltage was always kept low enough to prevent second order from being present at the wave-length used.

* *Ann. d. Phys.* xiii. (1922).
† *Zeitschr. f. Phys.* vii. (1921).

LI. *On the Longitudinal Elasticity and Poisson's Ratio of India-rubber.* *By* G. B. Deodhar, *M.Sc., Assistant Professor of Physics, Muir Central College, Allahabad*.*

Introduction.

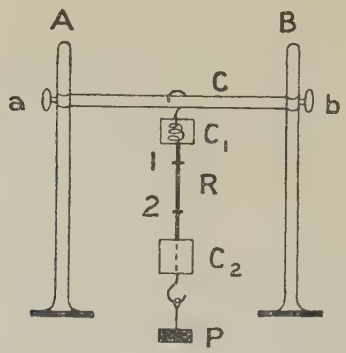
THE case of india-rubber owes much of its interest to the peculiar behaviour which it evinces when the operating load is put under different conditions of the substance. So far practically nothing is known of the constitution of india-rubber. A very intelligent attempt was made by Mr. Ono † to hit at a probable constitution of the substance by arriving at a theoretical formula for stress and strain, on certain assumptions, which would satisfy his experimental observations. But the very fact that he had to modify it to some empirical form points against his assumptions. It is most probably the extreme complexity of the constitution of india-rubber which is responsible for its striking behaviour at different temperatures and under various strains. The inversion temperature observed by A. E. Lundal ‡, the relation between elasticity modulus and temperature investigated by G. R. Dallander § and A. E. Lundal ‖, the elastic after-effect experimentally studied by J. C. Shedd and R. L. Ingersol ¶, and the relation between elongation and time for a particular pull investigated by P. Phillips** are some of the most interesting phenomena which are expected to throw some light on the molecular composition of india-rubber. However, it seems that very little has been done with a view to study experimentally the variation of the modulus of longitudinal elasticity with stretching. It is also very interesting to study whether in the face of varying modulus with stretching force Poisson's ratio really remains constant. A full study of these two phases of elastic strains in india-rubber would be a valuable help in the establishment of reliable elasticity equations. The present experiment was undertaken to study the elongation of india-rubber from the beginning of a finite strain up to the breaking point of the sample. It was also thought worth while to study Poisson's ratio over the whole range.

* Communicated by the Author.
† Proc. of Tokyo Math. Soc. vol. vii. (1913).
‡ Wiedemann's *Ann.* Dec. 1898, p. 741.
§ *Ofvers af Vet.-Ak. Forh.* xxviii. p. 703 (1871).
‖ *Loc. cit.*
¶ Phys. Rev. xix. pp. 107–116, Aug. 1904.
** Phil. Mag. ix. pp. 513–531 (1905).

Experimental Arrangement.

The experimental arangement is shown in the diagram, fig. 1. A and B are strong iron stands ; C is a horizontal iron bar clamped to A and B at *a* and *b*. C_1 and C_2 are small brass frames with corrugated grooves to hold the rubber piece R very firmly. P is a small weight-pan hung from a hook at the bottom of frame C_2. The whole suspension is suspended from the transverse bar C by a hook at the top of frame C_1. By putting weight on pan P any amount of tension could be applied to the rubber sample. The samples selected were pieces from rubber cords of circular cross-section. The diameter of the cross-section was obtained by

Fig. 1.



A & B, massive iron stands ; *a* & *b*, clamps ; C, a cross-bar of iron ; C_1 & C_2, brass frames to clamp rubber band R ; P, weight-pan.

taking the mean of several observations along the length of the cord. The measurements were made by a fine screw gauge reading up to 0·001 cm. Two fine marks 1 and 2 were made on the length of the cord, and the distance between the two was measured by a cathetometer kept at a distance. The distance between these two marks gave the length of a certain portion of the cord under various loads. The cathetometer could read up to 0·01 cm. As stretching under a definite pull is a function of time, the length corresponding to a particular load was measured some definite time after the application of each load. The temperature of the substance was 23°·0 C. and remained constant throughout the experiment. Any other sample could be substituted in place of the previous one simply by unscrewing the frames C_1 and C_2. The lengths were measured for increasing loads only, the observations being carried on up to the breaking point.

Observations and Discussion of Results.

A certain length of an old rubber cord was cut out and suspended as described above. The following table gives the cross-section and length of the sample corresponding to each load up to the breaking point.

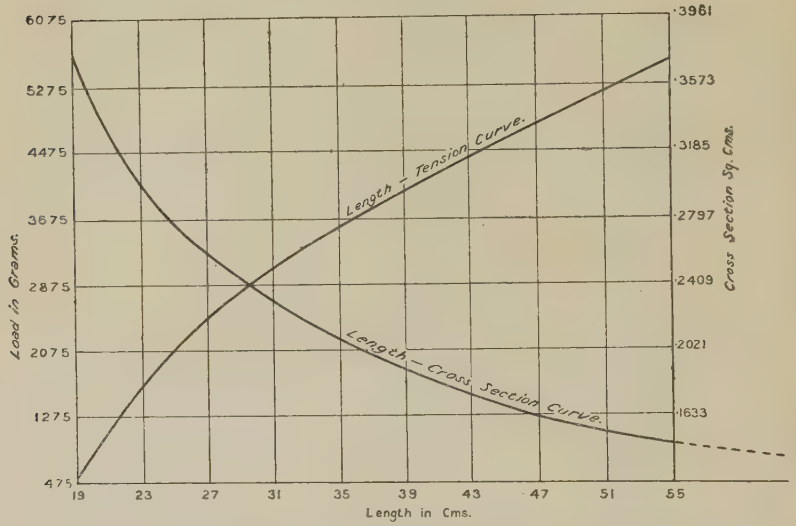
TABLE I.

Load.	Cross-section.	Length.
520 gms.	0·3771 sq. cm.	19·25 cms.
560 „	0·3692 „	19·38 „
600 „	0·3661 „	19·48 „
820 „	0·3524 „	20·12 „
970 „	0·3435 „	20·72 „
1120 „	0·3350 „	21·23 „
1320 „	0·3290 „	21·94 „
1520 „	0·3193 „	22·74 „
1720 „	0·3087 „	23·58 „
1920 „	0·2859 „	24·54 „
2120 „	0·2824 „	25·66 „
2320 „	0·2649 „	26·83 „
2520 „	0·2545 „	28·04 „
3020 „	0·2358 „	31·14 „
3520 „	0·1988 „	35·94 „
4020 „	0·1801 „	39·85 „
4520 „	0·1639 „	44·66 „
5020 „	0·1536 „	49·87 „

These observations were plotted on one graph paper and two curves, viz., length-tension curve and length-cross-section curve, were obtained (fig. 2). From the diagram it is seen that the cross-section of the material goes on decreasing logarithmically as the length increases. A close scrutiny of the length-tension curve shows that up to a point where the stretched length is about 5/4 times the original length a linear relation between length and tension holds good. Then, after that, there is a bend till the stretched length attains about twice the original value; after that, up to the breaking point a linear relation holds good again. The angles which the two linear portions make with the axis of lengths are different. From the inclinations of the lines it can be seen that over the range where the second linear relation holds good, a certain amount of load produces a greater elongation than that produced by the same load over the range where the first relation holds good. The second linear relation is more conspicuous than the first one as its range is larger.

The specimen was then taken out of the frames and another specimen was put in its place. This specimen was a certain length out of a new india-rubber cord. Observations

Fig. 2.



on this were taken in the same way as observations taken in the previous case. The general characteristic of the two curves are the same. For convenience I give below (Table II.) observations from 3000 grs. load and onwards up to the breaking point.

TABLE II.

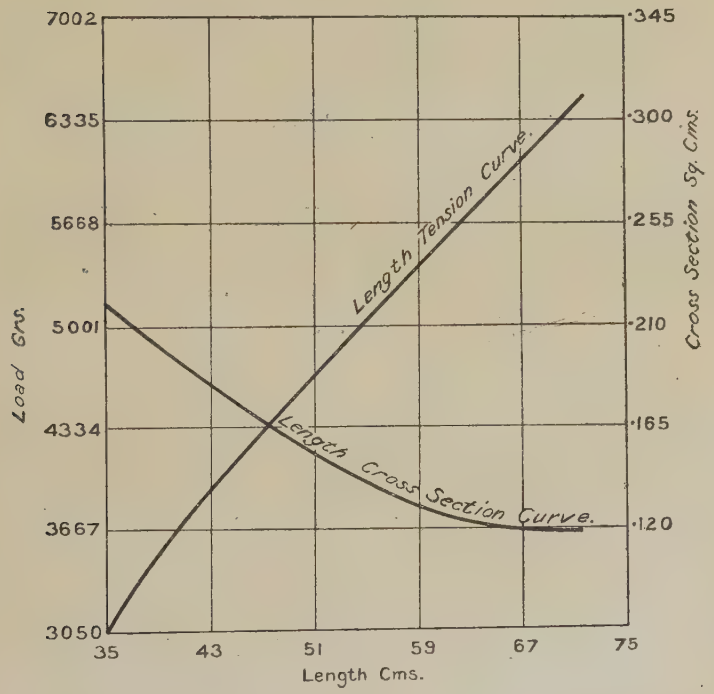
Load.	Cross-section.	Length.
*		
3000 gms.	0·2105 sq. cm.	34·89 cms.
3500 ,,	0·1949 ,,	39 07 ,,
3750 ,,	0 1900 ,,	41·01 ,,
4000 ,,	0·1800 ,,	43·84 ,,
4250 ,,	0·1670 ,,	47·02 ,,
4500 ,,	0·1597 ,,	48·91 ,,
4750 ,,	0·1520 ,,	52·20 ,,
5000 ,,	0·1479 ,,	54·82 ,,
5250 ,,	0·1390 ,,	57·61 ,,
5500 ,,	0·1341 ,,	60·16 ,,
5750 ,,	0·1300 ,,	63·20 ,,
6000 ,,	0·1280 ,,	65·88 ,,
6250 ,,	0·1220 ,,	68·81 ,,
6500 ,,	0·1204 ,,	71·70 ,,
6750 ,,	Broke	Broke

* Observations above this in original record.

The linearity after the bend is quite prominent in fig. 3.

In the case of india-rubber, unlike metals, any deforming force produces a finite stretching, and consequently the usual elasticity relations are not strictly applicable. However, if we take any two consecutive observations we should be fairly

Fig. 3.



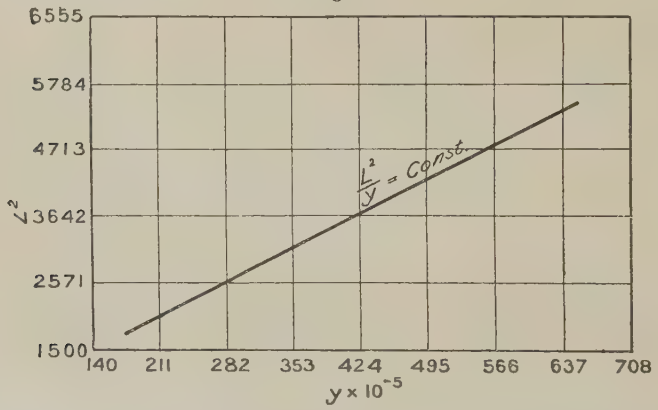
justified in applying Hooke's law. From Tables I. and II. values of Young's modulus were calculated, and it was found that the ratio of Young's modulus to the square of the stretched length over the two ranges where length-tension curve is a straight line, is a constant; while over the bend this constancy vanishes. The results for No. 2 are tabulated below.

TABLE III.

Stretched length L.	Young's modulus $y \times 10^{-5}$.	$\frac{L^2}{y} \times 10^5$.
39·07 cms.	149·9 dynes/cm.^{2}	0·098
41·01 ,,	152·0 ,,	0·091
43·84 ,,	182·1 ,,	0·094
47·02 ,,	222·0 ,,	0·101
48·91 ,,	243·6 ,,	0·102
52·20 ,,	280·0 ,,	0·103
54·82 ,,	280·5 ,,	0·093
57·61 ,,	360 0 ,,	0·108
60·16 ,,	402·2 ,,	0 111
63·20 ,,	452·0 ,,	0·113
65·88 ,,	492·9 ,,	0·110
68·81 ,,	550·0 ,,	0·116
71·70 ,,	611·0 ,,	0·118

From data in column 1 values of L^2 are calculated and these and data in column 2 of this table are plotted and the graph comes out to be a straight line (fig. 4).

Fig. 4.



This linear relation seems to be the most important feature of the elasticity of india-rubber, and any formula, theoretical or empirical, must bring out this relation in the initial and final stages of stretching. Mr. Ono * has obtained on certain assumptions the following theoretical formula :—

$$S_0 = A\lambda \left\{ 1 - \frac{2}{\lambda + \beta} \right\}, \quad \ldots \ldots \quad (1)$$

where A is a constant, λ = length ÷ length in natural state

* Proc. Tokyo Math. Soc. vol. vii. p. 39 (1913).

and β = breadth ÷ breadth in natural state. To suit his experimental observations he had to modify it to the following empirical form, which he says represents the relations between stress and strain very closely :

$$S_0 = A\left\{1 - \frac{2}{\lambda+\beta}\right\} \cdot e^{h(p-\lambda)^2} \quad . \quad . \quad . \quad (2)$$

where A, h, and p are constants and S_0 stress upon original cross-section. Now there are certain facts which tend to show that both the above equations are of doubtful reliability. In the first place, as pointed out on p. 475, a deforming force produces finite stretching in this case, and so it would be erroneous to refer a load always to the original cross-section and length and breadth respectively always to those in the natural state as done by Ono. Secondly, substituting the values of S_0, λ, and β in (1) should give us at least an approximate constant value of A. The following tables give the values of S_0, λ, β, and A calculated from Tables I. and II.

TABLE IV.

S_0.	λ.	β.	A.
3·7 kil. gr./cm.²	1·01	0·99	−731
3·9 ,,	1·01	0·98	−732
4·2 ,,	1·03	0·98	+844
4·6 ,,	1·04	0·98	442
5·1 ,,	1·06	0·98	249
5·4 ,,	1·09	0·97	171
5·8 ,,	1·11	0·95	100
6·5 ,,	1·14	0·95	100
7·3 ,,	1·19	0·93	107
8·1 ,,	1·25	0·91	87
8·8 ,,	1·31	0·88	79
9·6 ,,	1·36	0·86	70
11·5 ,,	1·52	0·83	50
13·5 ,,	1·75	0·76	38
15·3 ,,	1·94	0·71	31
17·2 ,,	2·23	0·69	24
19·1 ,,	2·43	0·68	22

Tables IV. & V. show that instead of being constant, A continually decreases with higher tensions. Substituting the values of A, λ, and β, we get a series of equations. Solving them by twos a number of values of h and p are obtained. It was found that there was no constancy in these values, showing that equation (2) is also not applicable. The

formulæ thus fail to satisfy experimental observations and the relation, $\frac{L^2}{y} = \text{const.}$, does not come out of them. Thirdly, a scrutiny of Ono's figures gives us that percentage discrepancy between the calculated and observed values of S_0 continually increases with higher tensions.

TABLE V.

(This table chiefly refers to the portion where $\frac{L^2}{y} = k$ holds.)

S_0.	λ.	β.	A.
22 $\frac{\text{kil. gr.}}{\text{cm.}^2}$	1·13	0·98	324
25 ,,	1·26	0·95	208
28 ,,	1·41	0·88	121
3. ,,	1·57	0·84	116
35 ,,	1·72	0·82	95
37 ,,	1·88	0·79	78
41 ,,	2·05	0·77	68

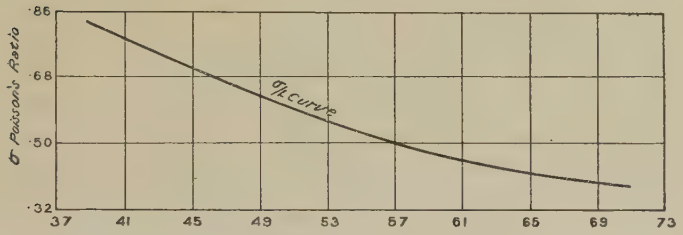
Poisson's ratio can be very easily calculated from data in Tables I. and II. It was found that this ratio is not a constant quantity but goes on decreasing with increasing length of the specimen. Some calculations are tabulated below and the data plotted on fig. 5 to bring out the relation between stretched length and Poisson's ratio.

Stretched length.	Poisson's Ratio.
39·07 cms.	0·87
43·84 ,,	0·77
48·91 ,,	0·63
54·82 ,,	0·54
60·16 ,,	0·48
65·88 ,,	0·42
71·70 ,,	0·38

This phenomenon together with the relation $\frac{L^2}{y} = k$ are of considerable interest since they are likely to throw some light on the nature of india-rubber, and would thus go a great way in establishing a general relation between stress

and strain by a rigorous mathematical treatment. The author hopes to obtain a general formula for elongation of india-rubber based on the theory of probability.

Fig. 5.



Summary.

In these experiments long and thick specimens were used. Variation of Young's modulus of india-rubber with load is experimentally studied, and it is found that there are two stages of stretching, initial and final, where $\frac{L^2}{y} = k$ holds good, L being stretched length and y Young's modulus. In the intermediate stages of stretching, that is during the changes where the length is between 5/4 and 2 times the original length, the above linearity breaks down.

The author's experimental results are not correctly represented by the stress and strain formula of Ono. It is found that Poisson's ratio for india-rubber is not a constant quantity as is generally supposed, but decreases with increasing length of the specimen.

Another relation between stress and strain is necessary which will satisfy the above experimental observations, and the author hopes to obtain it on the basis of the theory of probability.

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LII. *Notes on the Radiation and Ionization Potentials of the Rare Gases and on the Singlet and Enhanced Series of Argon.* *By* W. M. Hicks *.

IN my recently published 'Analysis of Spectra,' I have discussed certain difficulties in connexion with the radiation and ionization potentials of hydrogen and the rare gases. Within the last few months the results of several important experimental investigations have been made known, which support the suggestions there made. In the following notes these are considered, the hypothesis made is more fully considered and extended, and an attempt is made to determine the various series in argon on which its potentials depend.

Radiation and ionization potentials are those through which an electron must fall, in order respectively to make a gas radiate or to ionize it. In general, such potentials must give sufficient energy to dissociate the molecule, and then to act on the atom at one operation. In what follows, the word "true" is used to indicate the potentials required to produce radiation or ionization in the atom, when this is in its radiating configuration. Thus the "observed" ionization potential should be the sum of the dissociation potential and the "true" ionization. The word is also used in an analogous way as explained below in the discussion of the potentials of the rare gases.

Hydrogen.

Rad. $\left\{\begin{matrix}10{\cdot}5\\14\end{matrix}\right.$ Ion. $\left\{\begin{matrix}13{\cdot}6\\16{\cdot}9\end{matrix}\right.$ Dissoc. 3·3

1. In hydrogen two sets of potentials are observed, the lower corresponding to the "true" values. How is it, that in the molecular gas H_2, radiation and ionization can occur at their true or atomic values? In this case the true radiation (10·5) is about three times as large as the dissociation (3·3). Consequently, when the voltage has reached the true radiation value, each electron has sufficient energy to produce six atoms, any one of which may be made to radiate on impact by an electron possessing the full energy. But any such effect could not be recognizable unless the actual number of atoms present were an appreciable proportion of the whole gas. To explain this, it was supposed that the life of an atom, when formed, was long compared with ordinary molecular intervals—*e. g.* the life of an ion—but at that

* Communicated by the Author.

time there were no experimental data in support of the hypothesis. Since that was written, however, Wood * has produced evidence that an atmosphere of H takes about 1/5 second to change to H_2. This is an extremely long molecular interval, and should be sufficient to explain the persistence of a considerable proportion of H in an atmosphere of H_2 in which the electronic production of H per second just balances the recombination per second.

The Rare Gases.

2. In the rare gases the observed potentials are too large to represent the true values. No true voltages can be greater than those corresponding to N or 4N, according to the cases where the emitter is the atom or singly ionized (enhanced) atom. These voltages correspond to potentials of 13·54 and 54·16 respectively. Those of the gases hitherto observed—He, Ne, A—are considerably greater than these. This is not explainable by the existence of a dissociation potential, since here each molecule is already an atom. To meet this difficulty the suggestion was put forward that the ordinary atom in these gases is not capable of radiating in its normal condition, but requires some preliminary work to be done on it to change it into a configuration capable of emission. This supposition is supported also by the fact—at least proved in He—that the ordinary normal He atom does not absorb any of the He lines: in other words, it is not the actual emitter of these radiations. Further, it explains the absence of affinity between their own atoms or with those of other elements as due to the non-availability of their separable electrons. We shall indicate some evidence below that in Ne and A this change from the normal to the emitting states may take place in at least two stages. In discussing these gases it will be convenient to use symbols for these atomic configurations. We shall employ the following, in which a small dot represents a potential level, or position in the atom, a large dot an electron, and a - the nucleus :—

Normal atom	.●-●.	
1st prepared atom ..	.●-.●	or possibly ●.-.●
1st ionized atom ..	.●-..	,, ●.-..
2nd prepared atom..	●.-..	
2nd ionized atom ..	..-..	

* Phil. Mag. xlii. p. 729 (Nov. 1921).

3. On the suppositions that the He radiation involved is $HeP''(1)$—the strongest line,—and that the He^+ is that of $\lambda = 1216$ or $4N(1/2^2 - 1/3^2)$, the values of the various voltages required were found to be

1st prel. to raise one electron to radiating state	20·8 volts	
2nd prel. to raise the second, after 1st has been ejected .	45·7	„
True radiation potentials	$He = 1{\cdot}14$;	$He^+ = 7{\cdot}4$ „
True ionization potentials	$He = 4{\cdot}75$;	$He^+ = 13{\cdot}5$ „

or for observed values

Rad.: $He = 20{\cdot}8 + 1{\cdot}14 = 21{\cdot}9$; $He^+ = 66{\cdot}5 + 7{\cdot}4 = 73{\cdot}9$ volts
Ion.: $He = 20{\cdot}8 + 4{\cdot}75 = 25{\cdot}6$; $He^+ = 66{\cdot}5 + 13{\cdot}5 = 80$ „

It will be noted that the work to bring up the second electron after the first has been ejected is more than twice that required to bring up the first; which is to be expected.

Experimentally, radiation is also observed at 20·8, the first preliminary voltage. This means that, as in the analogous case of H, there should be a very considerable number of prepared atoms present when this voltage is reached. Consequently, here also a very long life must be postulated for the prepared atom when produced. This postulate and the value of 4·75 for the true ionization, are now confirmed by some striking experimental results by F. Kannenstine *.

He studies the potential current curves in an alternating unidirectional arc in helium at different frequencies. When the frequency is small—about 60 cycles per sec.,—the arc strikes when the potential rises to 28 volts and dies out when it falls to about 4 volts. As the measures are not exact, it is clear that the first refers to the complete ionizing potential, *i. e.* prel. + ion., but that, as the voltage falls back, the prepared atoms subsist in sufficient number to enable the arc to run with voltages down to about 4 volts, when it ceases. In other words, the ionizing potential of a prepared atom is about 4, which, allowing for observation uncertainties, agrees with the estimate of 4·75 found above from spectral

* Astro. Journ. lv. p. 343 (1922). Kannenstine refers to an apparently similar modified atom proposed by Messrs. Franck, Reiche, and Knipping, but the present writer has not yet been able to refer to their original paper, published in the new German periodical, *Zeitschrift für Physik*.

considerations. If the frequency, however, is just over 220 cycles per second, the striking of the arc occurs at 4 volts, which Kannenstine explains by the life of the "metastable" atoms overlapping the time of a cycle ; so that, when the potential again rises to 4 volts, there are sufficient prepared atoms still present to be ionized at 4 volts and to start the arc. The life must then be comparable with 1/220 sec.—a very long molecular interval.

In a second set of experiments, in a continuous current arc at 35 volts the potential was suddenly reduced. If the reduced potential was less than 3·5, the current died out immediately ; if just over, there were indications that it died out not instantaneously *. When the lower voltage rose to 22·6, the arc seemed to be maintained for a short time before dying out, and a further slight increase to 23·6 brought out another change in that the current died out in two steps. The first is clearly due to the persistence of prepared atoms. It may be suggested that the two steps are due to the two possible prepared atoms $\cdot\bullet-\bullet$ and $\bullet-\bullet$, the second requiring about 1 volt more than the first and having a shorter life. In the first continuance of the arc the current is carried by both forms ; then $\bullet-\bullet$ quickly changes to $\cdot\bullet-\bullet$ or $\cdot\bullet-\bullet\cdot$, and in the second step the current is carried by $\cdot\bullet-\bullet$. In Kannenstine's work we thus have the first experimental proof of the existence of a specially prepared atom different from the normal, of long life, and with an ionization potential in the neighbourhood of 4 volts.

The enhanced radiation of 73·9 has not—so far as the writer knows—been specially noted by any observer. It may be well, therefore, to consider in more detail the processes going on after the first ionization potential has been reached. For simplicity we shall take the two electrons as equivalent in the normal atom. Above 25 volts there may be present $\cdot\bullet-\bullet\cdot$, $\cdot\bullet-\bullet$, $\bullet-\bullet$, and even He^+ ; but as the life of an ion is probably short, the number of He^+ would be comparatively small, and their effect on enhanced radiation negligible. To make $\cdot\bullet-\bullet$ and $\bullet-\bullet$ radiate enhanced lines will require a potential of $4{\cdot}75+7{\cdot}4=12{\cdot}1$, so that the electron stream—now over 25 volts—could make a small proportion radiate in this way, and we should expect a small enhanced radiation effect, gradually increasing as the volts rise from 25 to 73. This will be superposed on a

* Possibly the self-induction in the circuit kept the initial voltage above 4·7 volts just after the lowering.

strong atomic or He radiation. Thus, even before the 73·9 is reached, there will be a growing and noticeable radiation of enhanced quality, and the increase of this at 73·9 may not be sufficiently marked to show the rate of change of the total. In other words, the direct radiation point of 73·9 would be smoothed out. Somewhat similar effects would ensue also at the ionization point, except that the total change produced by direct ionization would be much greater and the change at 80 volts distinctly marked.

The existence of two kinds of prepared atoms suggests a possible radiation difference. For instance, on the orbit theory of levels, the orbits must differ with what we may call different cores, as distinct from nucleus—*i.e.*, the "core" is the nucleus with internal electrons. Here there would be two kinds of cores, $\cdot\bullet\_\cdot\cdot\cdot$ and $\bullet\cdot\_\cdot\cdot\cdot$. We are tempted to take the second set of radiations as those of the HeP′. Now the difference of the two limits in P′ and P″ is

$$34853\ (\mathrm{He}'')-32033\ (\mathrm{He}')=6420,$$

which is equivalent to ·8 volt; and it is just this ·8 volt which Kannenstine's results as to the dying of the current in two steps suggest. With several stages in preparation, a larger number of these cores would be at disposal, and on this basis a larger number of sets might be expected in each spectral series type. Indeed, this seems to be actually the case in the other gases.

Neon *.

Rad. 11·8; 17·8. Ion. 16·7; 20·0; 22·8.

4. In neon we find (1) a second set of radiation and ionization potentials, 11·8, 16·7, with the same difference as the 17·8, 22·8, which appears after the volts have been raised beyond 22·8 and then backed; and (2) the existence of a third ionization potential 20·0, none belonging to Ne^+ radiators. The Ne^+ have not been investigated. The first phenomenon was explained on the same basis of the existence of long-lived prepared atoms after a sufficiently high potential had been exerted, but there still remained the difficulty that as this new potential was greater than 13·5 ($n>\mathrm{N}$), the radiation could not have been produced by a fully prepared atom. This, however, can be surmounted if more than one stage of preparation for gases beyond He exist—that is, for those possessing one or more sheath levels.

* Horton & Davies, Proc. Roy. Soc. xcviii. p. 124 (1920).

The second set of potentials in Ne may then be supposed produced direct from configurations ..●-.●. It may be interesting to attempt to obtain on this basis an estimate of the preliminary and other voltages for Ne, starting from Horton and Davies's * observations on the entrance of different lines as the voltage is increased. They are given with their several Zeeman patterns in the 'Analysis' (p. 213). In A and the heavier gases the preponderating system of lines belong to the triplet type, analogous to those of group II. In this system the lines relating to the potentials are two, $s'-p'$ and $s'-p_2'''$, corresponding therefore to the same ionization potential and two independent radiations. These series have Zeeman patterns respectively 0/1/1 and 0/3/2. Although in Ne these triplets either do not exist or are far down in the ultra-violet, we should expect corresponding singlet types to be related to the potentials, and we must look for strong lines corresponding to these types and having the above Zeeman patterns. Amongst those which Horton and Davies find as appearing at the lowest voltage are two lines with these patterns, viz. 5852 ($s_2 1-p_1 2$) and 6074 ($s_4 1-p_3 2$), the s, p referring to Paschen's allocations of types. But it must not be forgotten that there is evidence that the usual patterns exhibited by different series contain only the strongest components, some elements (*e. g.* Hg, Ba) showing additional ones. This would certainly be expected to be the case in Ne, which is notable for its complicated patterns. On this basis we should include also the lines

6402	s_5-p_9	0.1.2/6.7.8.9.10/6
6096	s_4-p_4	0.2/11.13.15/11,

which, omitting the components after the first, both reduce to 0/1/1, but no others reduce to 0/3/2. Now s_2, p_1, p_3, p_4 are subsidiary sequents, all link-connected, s_4, s_5 are the typical, and p_9 with p_8 the strongest of the p. Moreover, taking our assumption as to multiplicity of Zeeman pattern to be correct, the very numerous components in 6402 would seem to show that this is the representative of—at least—the chief $s'p'$ line. Provisionally we will take it so. Hence the limit is $s_5(1)=39887$; $p_9 2=24272$, so that the wave number of the line is 15615. These give for the true ionization potential 4·92 volts and true radiation 1·91. With the observed ionization of 22·8, this gives the first full preliminary potential $=17·9$. Hence the observed radiation potential should be $17·9+1·91=19·8$, whilst actually it is

* Phil. Mag. xli. p. 921 (1921).

17·8, which means that the radiation begins from the prepared atom at once. But this is what we have learnt to expect from a long-lived prepared atom. There ought to be a large increase of radiation at 19·85, but any such effect might possibly be masked by the existence of the additional ionization potential at 20 volts. We should expect a radiation potential due to the $s'p_2'''$ line (Z . P = 0/3/2). If the representative of this line is the doubtful 6074, the potentials would not be distinguishable from the others.

The "backed" set 11·8, 16·7 are 6·1 below the other. In other words, 6·1 volts have previously been applied. Thus the work to change the stage ..●-●.. to ..●-.●. is 6·1 volts, and to change the latter ..●-.●. to ..●-..● is 17·9 − 6·1 = 11·8. It may be just possible that the ionization potential of 20 may be that required to ionize the intermediate stage .●-.●.

An objection, which appears serious, may be raised to the choice of the lines taken as the potential representatives. In He, and as we shall see in A, the corresponding lines have each of their sequents (terme as Paschen calls them) both of order $m=1$, whereas the above-mentioned in Ne have one p_9 (indeed all the p limits), with $m=2$. We should certainly be surprised if Ne does not stand in line with the others. It might be explained by supposing that these $m=1$ lines exist, e. g., $p_9 = \mathrm{N}/(2{\cdot}12)^2$, so that the first order would be in the neighbourhood of $\mathrm{N}/(1{\cdot}12)^2$ or 87600, with negative n as in A and radiation potential of magnitude about $(87600 - 39887)/8100 = 5{\cdot}9$. But this again is out of step with He and A.

Argon.

Rad. 11·5. Ion. 15·1.

5. In argon a very doubtful attempt was made to illustrate the theory of the preliminary and true potentials by identifying two ultra-violet lines by Lyman as the representatives of $s'-p'$ and $s'-p_2'''$. At the time the author was under the impression that this ultra-violet spectrum belonged to the red. Reference, however, to Lyman's paper shows that it belongs to the blue, and that the red spectrum definitely has no prolongation into this region. Moreover, as will be shown later, one of the lines involved belongs to the enhanced or A^+ system. In the present note an attempt is made to obtain a more secure basis by first determining the singlet and enhanced series on which the lines related

to the potentials depend. This discussion is given in § 6 below.

The potentials 11·5 and 15·1 are those determined by Horton and Davies *. As other observers had obtained values for the ionization varying between 15 and 17, they returned to the problem, and they † have lately published the results of an investigation in which they simultaneously observed current changes and the first appearance and the intensity changes in the spectrum as the accelerating potential was increased. The first part of their paper deals with voltages up to 20 in which atomic radiations only enter. They find :

(1) the change in rate of increase of current at 11·5 is small ;

(2) there is a more marked change at about 15 ;

(3) at a few volts above 15, just over 17, there is a sudden sharp rise in current, and at this point the spectrum breaks out, showing lines belonging to the red spectrum.

They attribute this to increase of the electron stream due to neutralization of space electrification. One criticizes the conclusions of such experienced workers with some diffidence. But it is difficult to see how this space electrification can be neutralized without the entrance of + ions, which means the previous ionization of the gas. In other words, I would regard this new potential of 17+ as the real ionization, *i. e.* that at which an electron at one impact prepares the atom and ejects one of its electrons. It is the instant at which ionization is produced at one impact that the large effects are produced and the spectrum strongly appears. Space electrification is then diminished and the total electron stream is further increased, but it is a sequel and not a cause. With $17+x$ as the typical observed ionization, those originally observed at 11·5 and 15·1 would correspond to the analogous "backed set" in Ne, *i. e.* be due to direct impacts on atoms in one of the intermediate stages. The radiation from these less numerous centres would explain the slight increase of current observed at the 11·5 point. The preliminary potential would then be $17+x-$true ionization, in which the true ionization is to be determined from spectral data which we must now consider.

The lines observed by Horton and Davies all belonged to

* Proc. Roy. Soc. xcvii. p. 23 (1920).

† *Loc. cit.* cii. p. 131 (1922).

the red spectrum, and could be arranged in two categories. In one the intensities increased on backing for a time before the final decrease to extinction. In others they decreased continuously. Amongst the first set they give 4510, 4345, 4272. These are A_5, A_6, C_3 of Rydberg's Type II.* It is probable, therefore, that all of the set belong to this type. They seem to have some analogy to the secondary spectrum of H and the so-called band spectrum of He. Of the other category, 7067, 6967 are given as appearing amongst the first and gradually increasing with the voltage. On our supposition as to the nature of the lines associated with the potentials, they should belong to singlet series $s'-p'$, $s'-p_2'''$—of which, however, more than one set appear to be peculiar to the rare gases. The sets, however, are so near that the corresponding volt differences are inappreciable. The above two, for instance, only differ by ·02 volt. The line 6967 shows the normal triplet 0/1/1 corresponding to $s'-p'$. We shall adopt then 6965 as the required $s'-p'$, and 7067 as $s'-p_2'''$. The Zeeman pattern for 7067 has not been investigated, but there is also support for this allocation of type in the fact that there is a weak line 7029 (intens. 1 compared with 7 for 7067) at a separation of 75·28 ahead. Now the triplet separation ν_2 or $p_3'''-p_2'''$ is 75·6, the same within observation errors. In other words, there is evidence of the presence of a line $s'-p_3'''$ if the wave number is negative. Any such line should be weak. We shall take this indication that the wave number is negative. Therefore, using I. A,

$$\lambda = 7067{\cdot}218\ \dagger,$$

$$s'-p_2''' = -14145{\cdot}94.$$

Now, from the already known triplet series of A,

$$p_2''' = 51912{\cdot}28, \quad \text{whence} \quad s' = 37766{\cdot}34.$$

If this allocation is correct, it should be accompanied by other lines of the series $s'(1)-p_2'''(m)$ in the red spectrum, and possibly of the combinations $p'''(1)-p'''(m)$, involving p_1, p_2, p_3 in the blue spectrum. Unfortunately the values of $p'''(m)$, $m>1$, are not known directly, as the corresponding $P'''(m)$ lie in the ultra-violet far beyond any observed

* Query, are these Type II. really radiations from our supposed intermediate stages?

† Meissner, *Ann. d. Phys.* li. p. 115 (1916).

region. But a search shows that the series and combinations exist (see § 6 below). There is therefore converging and ample evidence that $\lambda=7067$ is the representative for $s'-p_2'''(m)$, and that consequently $s'=37766{\cdot}34$.

Passing now to $\lambda=6965{\cdot}432$ *, $n=14352{\cdot}62$, we must put

$$s'-p'=\pm 14352{\cdot}62,$$
$$p'=37766{\cdot}34\mp 14352{\cdot}62.$$

If 6965 is the representative of the first order of the series, as its great intensity indicates, p' corresponding to $m=1$ must be large, or the lower sign must be taken. This is supported also by the fact that a weak line 6870 exists which is separated from 6965 by the same amount, 206·7, as 6965 is from 7067. This exact agreement shows that 206·7 is a real relation, and consequently

$$s'-p'-(s'-p''')=p'''-p'=\pm 206{\cdot}7$$ or $s'-p'$ and $s'-p'''$

are of the same sign. Hence

$$p'=52118{\cdot}96.$$

Again, if this allocation is correct, other lines belonging to the series $s'-p'(m)$ should be found. This is so and also other lines corresponding to $p'-s'(m)$, combinations $s'(1)-s'(m)$, and indications of collaterals of $p'(1)-p'(m)$. For our present purposes we need only the first lines now considered fully established:

$$s'-p_2'''=-14145{\cdot}94, \qquad s'-p'=-14352{\cdot}65$$

with $\qquad s'=37766{\cdot}34, \qquad p'=52118{\cdot}96.$

But at present there is nothing to show whether those named s', p' should not be the typical p', s'. This would seem to be settled by the fact that the series $s'-p_2'''m$ is found, and not $p'-p_2'''m$. In other words, $s'=37760{\cdot}34$ is the limit which settles the ionization potential. There results

$$\text{true ion. potential}=377{\cdot}6684/81=4{\cdot}66.$$
$$\text{rad. potentials}=143{\cdot}526/81=1{\cdot}772,$$
$$=141{\cdot}459/81=1{\cdot}746,$$

whence the first preliminary potential

$$=17+x-4{\cdot}66=12{\cdot}3+x.$$

* Meissner, *Ann. d. Phys.* li. p. 115 (1916).

With our long-lived prepared atoms we should expect radiation to begin at this voltage, but any such radiation point would be smoothed out, in the way explained in the Ne discussion, by the presence of the radiation caused by direct impacts on the intermediate stage, and showing itself at 11·5.

The continuance of the spectrum on backing is explained as in He and Ne. With very intense electron streams the voltage could be reduced below 11·5 without the lines disappearing. The lowest value to which it could be backed was 6·5 volts. This denotes the value at which the lines ceased to be visible, so that the real limiting value would probably be slightly less. The theoretical limiting backing point is the "true" ionization potential or 4·7.

It is very desirable that Kannenstine's experiments should be extended to Ne, A, and the other gases. Our results show that it is probable that with sufficiently high frequencies, the arc would strike in A at 4·66 volts, and that it would die away in more than two steps.

We now pass to the consideration of the enhanced or A^+ potentials. There is no justification for the assumption sometimes made that the blue (or spark) spectrum is due wholly to ionized atoms. The blue spectrum comprises, with enhanced lines, also the typical triplet series, which always require a higher voltage to produce their lines than do their associated singlet systems. The latter, as we have seen, predominate in the red spectrum, which contains in addition the Type II. spectrum. With increasing voltage the lines of the triplet series in the blue spectrum should begin to appear, even before the second ionization is reached. The reason why Horton and Davies have not observed them is that none exist in the visible region in which their observations were made. The nearest is $D'''(1)$, $\lambda 4203$, or perhaps $F'''(3)$, about $\lambda 4980$, both outside. The first appearing should be $P'''(1)$, $\lambda 2344$, and afterwards $S'''(2)$, $\lambda 3765$. In the case of A^+ the line on which the potentials depend is the chief doublet line P_1''.

In extending their investigations they found that as the voltage further increased, the blue lines appeared at about 19 volts. "Their intensities increased as the voltage was raised from 19 to about 24 volts, after which it did not increase further until the voltage reached 34. From 34 volts up to 42 volts the blue spectrum lines increased very much in intensity." The increase in intensity was first noticeable

at 34 volts. Their tables * I., II., III. give a view of the appearance and change of intensities of these lines as the potential increased in steps of 2 volts from 19 to 42. The great increase after 34 is apparent at a glance. The lines they specially note as first appearing are λλ4430·4 and 4426·2, whilst the table shows 4348 as quite distinctly the first to appear, and the first to intensify. The sudden rise in intensity at 34 (especially in 4348) is a clear indication that atoms are now being doubly ionized at one electron impact. The entrance of the lines at 19 shows either that the real radiation potential has been reached, or that some of the numerous prepared atoms present are being made to radiate. Their fig. 5 would seem to show that the ionization potential must be close to 34·0. But it must not be forgotten that the gas contains now a very large proportion of prepared atoms, and that 34 volts may refer to their ionization, and that the normal atom might require a higher voltage.

For further progress it is necessary to know the enhanced doublet series in this element, which have not yet been allocated. An attempt to do so is made in § 6 below. For reasons there given, I do not feel complete certainty in the correctness of the allocation, although the three arrangements for S″, P″, D″ hold well together. A complete test is difficult because the higher orders run down into the far ultra-violet, and especially because a knowledge of the Zeeman patterns for the lines in question is wanting. The result is that the first-order P″ lines are (Kayser's measures) :

	λ(R.A.).	I.	*n*.	
$P_2(2)$	4426·165	8	22586·70	404·87
$P_1(2)$	4348·222	9	22991·57	

with the limit $P_1(\infty) = 80965$.

With these allocations we find

$$\text{true rad. pot.} = 222{\cdot}91/81 = 2{\cdot}84,$$
$$\text{true ion. pot.} = 809{\cdot}65/81 = 9{\cdot}25.$$

With the observed ionization at 34, the preliminary potential, *i. e.* that required to eject one electron and raise

* For our purposes these tables should be regarded as one. Stark's categories indeed almost certainly comprise lines emitted by related configurations, but any definite interpretation of their state of ionization involves many difficulties ('Analysis of Spectra,' p. 111). It is generally understood that Stark himself has now somewhat modified his views.

the other to the radiating stage, is $34{\cdot}0-9{\cdot}25=24{\cdot}8$. All this is on the assumption that 34 volts is that required to fully ionize the normal atom ..●-●... As it takes $17+x$ volts to produce A^+, it leaves $7{\cdot}8-x$ as the work required to raise the second electron to the radiating state after the first has been ejected: in other words, less than to raise the first when the second is present. We should expect it, as in He, to be more than double. This is an indication that the 34 volts potential does not refer to ionization of the normal atom at one electron impact, but to ionization of the atom at an intermediate stage. The real ionization of the atom to A^{++} must be at a few volts above $17+2\times17$, or greater than 51. It is, of course, possible that before this potential has been reached the greater proportion of the normal atoms may have been transformed into intermediate stages, especially that represented by the fully prepared atom ●..-..●, in which case no increase of ionization would be apparent at this highest voltage. We should scarcely expect a long life for the A^+ atom, either .●-... or ●.-..., so that the proportion present would not be large except for intense electron streams. It would account, however, for the first faint appearance of enhanced radiation at a little over 19 volts. With several possible stages it is impossible to say in detail what would happen without a knowledge of their various lives. But it may be suggested that the 34 volts may be due to the ionization of .●-... produced by preparatory +ion. pot., supposing the preparatory voltage for the second preparation after the first electron is ejected is somewhat larger than twice the first preliminary. If this be $2(12{\cdot}3+x)$, we should require

$$24{\cdot}6+2x+9{\cdot}25=34,$$

$$x=\cdot07.$$

Nothing is to be gained at present by attempting a more intimate analysis.

The singlets and doublets of argon.

6. The triplet separations in A are $\nu_1=179{\cdot}50$ and $\nu_2=75{\cdot}60$. The limit of the S_1 series, as determined from the first three lines, is *51731·05* R/A, whence $S_2(\infty)$ or $p_2'''(1)$ is 51912·28 I/A. The first and third orders lie in the ultraviolet with considerable possible observation errors, so that 51912 is subject to an uncertainty of a few units. In fact,

the value * as deduced from the difference and summation series F and **F**, give it about 2 larger.

The problem of determining the singlet series is complicated by the suspicion that these gases possess several sets of each type and by the certainty that displacement is very prevalent. Many of the red lines appear disrupted into several collaterals in the blue. Also these singlets in general do not appear very amenable to the usual formulæ. We have the direct evidence, however, indicated above, for the $P'(1)$ and $s'1-p_2'''1$, and thus get secure starting-points. The lines given in the following tables for S′, P′ appear to form at least one set of related series. The O−C are not large compared with the possible, and are considerably diminished if the limits are taken a few units larger, as indicated above. But there are peculiarities. Whilst the combination $p'1-p'2$ is not a good agreement (displacement 10), there is a very close one for a sort of satellite to $p'(1)$, $n=14410{\cdot}4$, and the same line serves as the first of a $p'1-\sigma'm$ set which form combinations with the s'. In general, in the successive orders of the $p'''m$, the values of the $\triangle$ are very nearly the same or between $\triangle$ and $\cdot 8\triangle$. It is thus easy to obtain approximate estimates of the values of the p''' separations for different orders although the lines themselves are not known. Here $\triangle_1=2519$, $\triangle_2=1057$, and the resulting ν_1, ν_2 for $m=2$, 3 with the same $\triangle$ are

$m=2$	$\nu_1=37{\cdot}37$	$\nu_2=15{\cdot}70$
$m=3$	$\nu_1=13{\cdot}40$	$\nu_2=\ 5{\cdot}63$

and *may* be somewhat less. It will be seen that these appear in the combinations $p'''1-p'''m$. These series deserve a more exhaustive investigation in connexion with a comparative study of the same series in the heavier gases. But it is too large a question for the present note. The important point here is the support they give to the allocation of the first lines $P'(1)$ and $s'1-p_2'''1$.

In the enhanced doublet series, the P, S, D series, with $\nu=404{\cdot}63$ appear to hang well together, with formulæ of normal types, as well as representatives of the $p''2-p''3$ combinations. There is evidence of a large number of related sets shown by the large number of the 404 separations in the spectrum. The normal ν separation for this type has a value a little larger than twice the triplet ν_1—here 360—for which 404, although rather large, may serve. But perhaps the more significant relation is that in enhanced series in group II the mantissæ difference on which ν depends is always about

* Trans. Roy. Soc. ccxx. p. 446.

the same as the triplet $\triangle_1 + \triangle_2$, here 3576. But with the limit here used, $S_1(\infty) = 63973$, the difference required is 8243, of the order of 143δ, far exceeding the value of the oun multiple known for any other case. The 3576 would produce a separation of about 180. I suspect, therefore, that the actual limit of the true series is much larger, with this $3576 + ?$ producing $\nu = 404$. In that case the series here adopted would be linked to normal ones †, and the formula for pm would be different. Further, many of the lines are attached to others by triplet links, of the possibility of which between enhanced and triplet series we have no experience. The matter must be left for further discussion before complete certitude of the correctness of the allocations can be felt.

In the tables, measures in R.A are printed in italics. Small brackets after numbers or below the tables refer to the references immediately following this. Numbers enclosed in square brackets are calculated values. r, b refer to the red and blue spectra respectively.

References.

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2. J. M. Eder and E. Valenta.—*Denks. Wien. Akad.* lxiv. p. 216 (1896).
3. T. Lyman.—Spectroscopy of extreme ultra-violet.
4. K. W. Meissner.—*Ann. d. Phys.* li. p. 115 (1916).
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Table I.

m.	P′ $\sigma'(1) - p'm$ I.	λ.	n.	$d\lambda$.	S′ $p'1 - \sigma'(m)$ I.	λ.	n.	$d\lambda$.
1	8	6965·432 [1] r	−14352·65	*	8	6965·432 r	14352·65	*
	1	*6937·8 r*	−14410·4		1	*6937·8 r*	14410·4	
2	5	*5188·46* [1] r	19268·91	*	4	*2692·8 b*	37126·6	*
					8	*2708·40 b*	36912·64	
3	2	*3514·513 r*	28446·43	−·3	3	*2265·2 b*	44134·2	−·27
					2	*2263·0 b*	44177·1	
4	...	...	[32133·80]		1	*2120·0 b*	47156·7	·3
5					1	*2059·5 b*	48751·8	−·23
	1 a (4); 1 b, 2, 3 (1).				1 a (4); 2...5 (2); 1 b (1).			

[1] Zeeman Patterns, 0/1/1.

† Such parallel sets are the rule in the triplet systems of Kr, X.

Combinations.

No $s'-s'm$, but

$s'1-\sigma'2$	3	*4431·172* (1) *b*	22561·93	[... 60·0]
$s'1-\sigma'3$	2	*3352·248* (1) *b*	29823·32	[... 24·68]
$\sigma'1-s'2$	5	*4401·156* (1) *b*	22715·81	[... 16·2]
$\sigma'1-s'3$?	1	*3361·973* (1) *b*	29737·05?	[... 23·9]+13
$\sigma'1-s'4$	3	*3054·846* (1) *b*	32726·64	[... 24·0]
$p'1-p'2$?	1	*2972·60* (1) *r*	33632·07?	[... 621·56]+11
$p'1-p'3$	beyond obs. in red.			
$\varpi'1-p'2$	2	2968·39 (1) *r*	33679·78	[... 9·27]

all measures by (1).

$$P'=37766{\cdot}34-N/\{m+{\cdot}419427+{\cdot}031228/m\}^2,$$
$$S'=52118{\cdot}99-N/\{m+{\cdot}705374-{\cdot}001260/m\}^2.$$

Table II.

	$s'1-p_2'''m.$				$s'-\varpi_2'''m.$		
$m.$	I.	λ.	$n.$	$d\lambda.$	I.	λ.	$n.$
1	7	7066·218 *r*	−14145·94	*			
	1	*7029·2*[1] *r*	−14223·0				
2	2	*5010·4*[2] *r*	19953·7	*	4	*4965 239 b*	20135·17
3	2	*3476·894 r*	28754·52	1·46[3]	2	*3464·364 b*	28858·18
4	...	...	[32338·82]				
	1 *a* (4); 1 *a*, 2, 3 (1).				2, 3 (1).		

[1] is $s'1-p_3'''1$.

[2] This line is omitted by Kayser in his Handbuch. The value as given in the blue spectrum is *5009·426*, $n=19957{\cdot}57$. It agrees better with the combinations below.

[3] *or* the line is $s'-p_1'''(3)$.

Combinations (the ''' are omitted).

$p_2 1-p_2 2$	3	*2931·52* (1)	34103·36	**79·74**	[... 3·51]
$p_3 1-p_2 2$	4	*2924·68* (1)	34183·10		
$p_2 1-p_2 3$	not obs.		[42911·32]	**14·2**	
$p_2 1-p_1 3$	3	*2339·9* (2)	42725·51		[... 24·72]
$p_2 1-p_2 4$	2	*2151·2* (2)	46472·7	**174·2**	[... 84·76
$p_1 1-p_1 4$	1	*2159·3* (2)	46298·5		[... 310·7 **174·0**]

The obs. $m=4$ are 12 behind the calculated.

$p_1 1-\varpi 2$	3	*2931·52* (1)	34103·4	**179·6**	
$p_2 1-\varpi 2$	2	*2916·3* (2)	34283·0		[... 81·1]
$p_2 1-\varpi 3$	1	*2324·7* (2)	43004·4		[... 4·12]

$$p_2'''(m)=N/\{m+{\cdot}509272-{\cdot}055732/m\}^2.$$

S″. TABLE III. D″.

m.	I.	λ.	n.	$d\lambda$.	m.	I.	λ.	n.	$d\lambda$.
2	9	*4348·222*	*−22991·57*	*	2	3	*6644·2*	*−15046·64*	
	8	*4426·165*	*−22586·70*			3	*6699·06*	*−14923·41*	*
						1	*6827·83*	*−14641·98*	*
3	5	*4430·355*	*22565·34*	*					
	4	*4352·368*	*22969·67*		3		...	[24850·3]	
						7	*4014·002*	*24905·89*	*
4	3	*2512·3*	*39792·4*	*		3	*3958·529*	*25254·91*	*
	1	*2487·0*	*40197·1*						
					4		...	[40733·71]	
5	1	*2077·2*	*48126·6*	·13		1	*2453·0*	*40754·3*	·5
			[*48531·30*]			2	*2430·1*	*41138·4*	·03
6	...	...	[*52792·47*]		5	...	...	[48603·83]	
								[48614·8]	
								[49008·4]	

2, 3 (1); 4, 5 (2). 2*a*, 3 (1); 2*b*, *c* (5); 4 (2).

$\nu = 404{\cdot}63.$

$$S_1(m) = 63973{\cdot}65 - 4N/\{m + {\cdot}272739 - {\cdot}053466/m\}^2,$$
$$D_{11}(m) = 63973{\cdot}65 - 4N/\{m + {\cdot}336896 + {\cdot}042312/m\}^2,$$
$$D_{12}(m) = 63973{\cdot}65 - 4N/\{m + {\cdot}333436 + {\cdot}045552/m\}^2.$$

TABLE IV.

P″.

m.	I.	λ.	n.	ν.
2	8	*4426·165*	*22586·70*	**404·87**
	9	*4348·222*	*22991·57*	
3	9	*1855·7*	*53870·3*	**160·4**[1]
	4	*1850·2*	*54030·7*	
4	...	...	[*66808·5*]	
			[*60728·9*]	

2 (1); 3 (3).

[1] Abnormal separation, should be 150 or less, and intensities abnormal.

Combinations.

$p_1 2 - p_2 3$	2	*3237·920* (1)	*30875·30*	**150·8**	[... 78·7]
$p_1 2 - p_1 3$	1	*3222·183* (1)	*31026·10*	**418·46**	[39·1]
$p_2 2 - p_1 3$	1	*3179·30* (2)	*31444·56*		[43·7]
$p_2 2 - p_2 3$	3	*3194·440* (1)	*31295·93*	**148·6**	[83·6]

The normal separation for $m=3$ is 147 or less. That for $m=3$ of 160 is excessive and is due to displacement. The combinations show the normal values. These combinations show that the displacement is in $p_1(3)$ causing a shift of 13, say $p_1(3)(+x\delta)$, x about 12. Then in the second combination $p_1 3$ is normal, in the third it is $p_1(3)(x\delta)$, and in the fourth the same displacement is continued in p_2 and is $p_2(3)(x\delta)$. This displacement in $p_1(3)$ will affect the constants in the formula for $P_1(m)$:

$$P_1(m) = 86965{\cdot}22 - 4N/\{m + {\cdot}711777 - {\cdot}186144/m\}^2,$$
$$P_2(m) = 86965{\cdot}22 - 4N/\{m + {\cdot}701675 - {\cdot}182466/m\}^2.$$

December 8, 1922.

LIII. *Thermodynamics and Statistical Mechanics.* By R. H. Fowler, *M.A., Fellow and Lecturer in Trinity College, Cambridge* *.

§ 1. *Introduction and Summary.*—In a series of papers † a method has been developed for calculating the distribution laws for assemblies in statistical equilibrium. The more general case is treated in the third paper, which deals with assemblies in which dissociation can take place. All the results obtained are proved purely as theorems in statistical mechanics based on the general principles of the quantum theory, and include the laws of dissociation-equilibria in perfect gases and of the vapour-pressure of crystals. No appeal is made at any stage to thermodynamic arguments—a feature which may legitimately be claimed as an advantage in molecular statistics.

The equilibrium conditions of statistical mechanics are in general independent of the molecular mechanisms by which exchanges of energy are effected. It is not until the study of reaction velocities and analogous problems is taken up that the molecular mechanisms themselves become really of first-class importance. In spite of this limitation, the theory of statistical equilibrium does take one a definite step beyond the field of classical thermodynamics, and for the systems to which it is applicable it must imply thermodynamical laws. It is therefore of some interest and importance to deduce the laws of thermodynamics from the theory of statistical equilibrium with the widest possible generality. This is especially the case for the third law—*i. e.*, Nernst's Heat Theorem,—as Ehrenfest and Trkal ‡ point out in a very interesting paper on this subject which is quoted extensively in the third paper. We have already done this for certain assemblies in which the number of individual systems of every type is fixed §. It is now possible to extend the argument to assemblies in dissociative equilibrium.

* Communicated by the Author.

† Darwin and Fowler, Phil. Mag. xliv. pp. 450, 823 (1922); Fowler, Phil. Mag. xlv. p. 1. These will be cited as first, second, and third papers respectively.

I take this opportunity of expressing my indebtedness to Mr. Darwin, whose share in the work is really by no means confined to the two papers written in collaboration. Mr. Darwin, however, must not be held responsible for any erroneous statements which may be found here.

‡ Ehrenfest and Trkal, Proc. Sect. Sciences Amsterdam, vol. xxiii. p. 162 (1920).

§ Darwin and Fowler, Second paper.

The paper just referred to starts with a critical examination of the usual presentation of entropy in statistical mechanics. We were forced to conclude that a proper logical account of entropy starting from the well-known hypothesis of Boltzmann is, if possible at all, necessarily somewhat recondite, and that the most satisfactory method is to use the classical equation $d\mathrm{Q}=\mathrm{T}d\mathrm{S}$ in the classical way. The idea of entropy in statistical mechanics seems, in fact, to be of secondary importance, and can usually, if not always, be dispensed with altogether. It is unnecessary to repeat this discussion, which applies with at least equal force to the dissociating assemblies considered here. We shall accept the results and define the entropy of a dissociating assembly in the first instance by the classical equation.

The contents of this paper are briefly as follows:—After summarizing in § 2 such of our previous results as are relevant, we prove in § 3 that for dissociating assemblies in statistical equilibrium it is possible to define functions S and T which satisfy the equation $d\mathrm{Q}=\mathrm{T}d\mathrm{S}$ and have all the properties essential to entropy and absolute temperature in thermodynamics. Incidentally we thus establish in the only completely logical way the relation between the empirical temperature ϑ and the absolute temperature T for such assemblies*. We obtain expressions for the entropy of the various groups of systems in the assembly which depend in a definite way on the number of systems in any group. In § 4 we show how the connexion with thermodynamics can alternatively be made by means of Planck's Characteristic Function. Up to this point we have assumed the point of view to which we were led by the discussion of the second paper. In § 5 we reopen parts of this discussion and examine shortly possible definitions of entropy for dissociating assemblies in connexion with the increasing property. This property is deduced in § 6 for entropy, suitably defined, from the characteristics of statistical equilibrium.

We have thus shown that there exists for the assemblies with which we deal a function of their state, the entropy, with all the requisite thermodynamic properties. The laws of Thermodynamics and their consequences are therefore

* We have insisted that the ideas of thermodynamics are of secondary importance in statistical mechanics. Here, in the logical introduction of T, they are, however, necessary; this is natural, for the *absolute* temperature scale is essentially a thermodynamic idea.

true for such assemblies. We show further, in § 7, that Nernst's Heat Theorem must also be true for them. It is a direct consequence of the characteristics of statistical equilibrium, on one condition—that the weights of the lowest quantum states of the reacting systems are equal. There is every theoretical reason to suppose that this condition is fulfilled by all condensed systems, or at any rate by all crystals. In this way, this theorem and the resulting properties of the chemical constants can be placed in their true perspective as theorems in statistical mechanics. It is not necessary to postulate the existence of entropy at any stage in the argument.

The general object of the paper is to amplify the discussion of our second paper with the help of the additional theoretical material now available.

§ 2. *Summary of previous results.*—The essential features of our method—the calculation of *average* values, the idea of weight, the use of partition functions (Planck's "Zustandsumme" in another form), and the complex integral for the total number of weighted complexions representing the assembly—are expounded in the first two papers and fully summarized in the third. They must be taken for granted here without further introduction. We must recall, however, the notation and formulæ. It will be sufficient to give these in their general form applicable to cases of dissociation.

Consider an assembly with $M_1 \ldots M$ free atoms and $N_1, \ldots, N_j$ free molecules. Let $g_1(z), \ldots, g_s(z)$, $h_1(z), \ldots, h_j(z)$ respectively be their partition functions for the kinetic energy of translation and potential energy in any external fields of force. Let $b_1(z), \ldots, b_j(z)$ be the partition functions for the rotational and vibrational energy (internal) of the molecules. The potential energy depends on certain parameters $y_1, y_2, \ldots$ defining the external fields of force. The walls of the enclosure containing the assembly can be regarded as the limit of intense local fields of force, and are thus included above. We can only consider the case in which each type of gas is perfect, and then

$$g(z),\ h(z) = \frac{(2\pi m)^{3/2}\,\mathrm{V}}{h^3\,(\log 1/z)^{3/2}}, \quad . \quad . \quad . \quad . \quad (2{\cdot}1)$$

where m is the mass of, and V the volume * of the container

* The volume can be different for the different atoms and molecules if some of the walls are semi-permeable.

available to the atom or molecule concerned. Let E be the energy of the assembly, supposed zero when all the molecules are dissociated and the resulting atoms all at rest in a field of potential zero. E so defined can be negative, but that is of no account. Let $\chi_1, \chi_2, \ldots$ be the energies required to dissociate the respective molecules, at rest in their lowest quantum state, into their individual atoms at rest. Then the number of weighted complexions c of any one example of such an assembly is

$$c = \frac{1}{2\pi i}\int_\gamma \frac{dz}{z^{E+1}}[g_1(z)]^{M_1}\ldots[g_s(z)]^{M_s}\left[\frac{h_1(z)b_1(z)}{z^{\chi_1}}\right]^{N_1}\ldots \times\left[\frac{h_j(z)b_j(z)}{z^{\chi_j}}\right]^{N_j}. \quad (2{\cdot}2)$$

The integral is taken round a contour γ, which is any circle with its centre at $z=0$ and radius less than unity. The number of different examples of such an assembly with the same M's and N's is *

$$\frac{X_1!\ldots X_s!}{M_1!\ldots M_s!\ N_1!\ldots N_j!\ \sigma_1^{N_1}\ldots\sigma_j^{N_j}}, \quad (2{\cdot}21)$$

where $X_1, \ldots, X_s$ are the total number of atoms of each type (including those in the molecules) and $\sigma_1, \ldots, \sigma_j$ are the symmetry numbers of the molecules. The number of weighted complexions representing a specified statistical state of the assembly in which there are $M_1, \ldots, M^s$ atoms and $N_1, \ldots, N_j$ molecules of each type is therefore

$$\frac{X_1!\ldots X_s!\ c}{M_1!\ldots M_s!\ N_1!\ldots N_j!\ \sigma_1^{N_1}\ldots\sigma_j^{N_j}}. \quad (2{\cdot}22)$$

If the rth molecule contains $q_{1r}\ldots q_{sr}$ atoms of the various types, then

$$X_t = M_t + \Sigma_r q_{tr}N_r, \quad (t=1, \ldots, s), \quad (2{\cdot}23)$$

and the total number of weighted complexions for the assembly in any state (with given energy E) can be put in the form

$$C = \frac{1}{2\pi i}\int \frac{dz}{z^{E+1}}[g_1(z)]^{X_1}\ldots[g_s(z)]^{X_s} \times\Sigma_{(N)}\frac{X_1!\ldots X_s!\ \beta_1^{N_1}\ldots\beta_j^{N_j}}{M_1!\ldots M_s!\ N_1!\ldots N_j!}. \quad (2{\cdot}24)$$

* Ehrenfest and Trkal, *loc. cit.* p. 169.

where

$$\beta_r = \frac{h_r(z)\, b_r(z)}{\sigma_r{}^{z\chi_r}\{g_1(z)\}^{q_{1r}} \ldots \{g_s(z)\}^{q_{sr}}}, \quad (r=1, \ldots, j). \quad (2{\cdot}25)$$

The summation $\Sigma_{(N)}$ is taken over all possible values of the N's from zero (included) to the largest values which leave all the M's positive or zero.

The conditions of statistical equilibrium follow at once. We find that $C\overline{N}_r$ is given by an integral identical with (2·24), except for the addition of a factor N_r under the summation sign $\Sigma_{(N)}$. After evaluation, we find that the equilibrium values $\overline{M}_1, \ldots, \overline{M}_s, \overline{N}_1, \ldots, \overline{N}_j$ are determined uniquely by the equations

$$\frac{\overline{N}_r}{(\overline{M}_1)^{q_{1r}} \ldots (\overline{M}_s)^{q_{sr}}} = \beta_r(\vartheta), \quad (r=1, \ldots, j), \quad . \quad (2{\cdot}3)$$

combined with (2·23), provided that ϑ is determined as the unique root of the equation

$$E = \Sigma_t X_t \vartheta \frac{\partial}{\partial \vartheta} \log g_t(\vartheta) + \Sigma_r \overline{N}_r \vartheta \frac{\partial}{\partial \vartheta} \log \beta_r(\vartheta), \quad . \quad . \quad (2{\cdot}4)$$

$$= \Sigma_t \overline{M}_t \vartheta \frac{\partial}{\partial \vartheta} \log g_t(\vartheta) + \Sigma_r \overline{N}_r \vartheta \frac{\partial}{\partial \vartheta} \log \{h_r(\vartheta)\, b_r(\vartheta)\} - \Sigma_r \overline{N}_r \chi_r. \quad (2{\cdot}41)$$

The quantity ϑ may be identified with the empirical temperature.

The foregoing equations still hold good if the assembly contains other systems which can share its energy besides the dissociating and associating free atoms and molecules. The only difference then is that the partition function for the additional systems appears as a factor in the integrand of (2·2) and of (2·24) outside the summation sign, and gives rise to an extra term in (2·4) and (2·41). We can in this way, for example, include the energy of the temperature radiation in the assembly. The results as functions of ϑ are unaffected.

Similar arguments apply to a crystal in equilibrium with its own vapour, if we may suppose that the partition function for the crystal of M molecules can be put in the form $[K(z)]^M$ *. If χ is now the work required to

* That this form is possible follows from Born's work. See Darwin and Fowler, Proc. Camb. Phil. Soc. vol. xxi. p. 262.

remove one molecule from the crystal in its lowest quantum state, and leave it at rest as a free molecule in its lowest quantum state, then the number of weighted complexions representing one example of such an assembly is

$$c = \frac{1}{2\pi i}\int_\gamma \frac{dz}{z^{E+1}}[K(z)]^M[b(z)\,h(z)z^\chi]^N. \quad . \quad . \quad (2{\cdot}5)$$

The number * of examples of the assembly is

$$\frac{X_1!\ldots X_s!}{N!\,\sigma^N}. \quad . \quad . \quad . \quad . \quad . \quad (2{\cdot}51)$$

If the total number of molecules is X (=M+N), then the total number of complexions representing the assembly (X large) is proportional to

$$C = \frac{1}{2\pi i}\int_\gamma \frac{dz}{z^{E+1}}[K(z)]^X \exp\left\{\frac{b(z)\,h(z)\,z^\chi}{\sigma K(z)}\right\}, \quad (2{\cdot}52)$$

and

$$\bar{N} = \frac{b(\vartheta)\,h(\vartheta)\,\vartheta^\chi}{\sigma K(\vartheta)}, \quad . \quad . \quad . \quad . \quad . \quad (2{\cdot}53)$$

provided ϑ is determined by the equation

$$E = X\vartheta\frac{\partial}{\partial\vartheta}\log K(\vartheta) + \vartheta\frac{\partial\bar{N}}{\partial\vartheta}. \quad . \quad . \quad (2{\cdot}54)$$

The distribution laws for either of these assemblies can be shown to be the same as if the values of the M's and N's were permanently fixed at their equilibrium values. The generalized force component † Y_1 tending to increase the coordinate y_1 of the bodies (walls) external to the system is

$$\bar{Y}_1 = \frac{1}{\log 1/\vartheta}\left\{\Sigma_t\bar{M}_t\frac{\partial}{\partial y_1}\log g_t + \Sigma_r\bar{N}_r\frac{\partial}{\partial y_1}\log(h_r b_r)\right\}. \quad (2{\cdot}6)$$

§ 3. *The entropy of an assembly in dissociative equilibrium.*—We shall show in this section that the assemblies of § 2 obey the laws of classical thermodynamics by showing that functions S and T exist satisfying the equation $dQ = Td\mathrm{S}$.

* The number may differ from this by a constant factor which is irrelevant here. The X's are the total numbers of atoms composing the molecules. We must think of dissociation exchanges as still theoretically possible, in order to extend fully the trajectory of the assembly.

† Second paper, § 7.

We take first the assembly of dissociating perfect gases. By the definition of $d\mathrm{Q}$ we have for any assembly,

$$d\mathrm{Q} = d\mathrm{E} + \Sigma \mathrm{Y} dy.$$

Formula (2·6) can be written in the form

$$\mathrm{Y}_1 = \frac{1}{\log 1/\vartheta}\left\{\Sigma_t \mathrm{X}_t \frac{\partial}{\partial y_1}\log g_t + \Sigma_r \bar{\mathrm{N}}_r \frac{\partial}{\partial y_1}\log \beta_r\right\}. \quad (3{\cdot}1)$$

The reduction to (3·1) follows at once from the fact that σ and ϑ^{χ_r} are necessarily independent of the y's. Further, by (2·4), $d\mathrm{E}$ can be written in the form

$$d\mathrm{E} = \left[\Sigma_t \mathrm{X}_t \left\{\frac{\partial}{\partial \vartheta}\log g_t + \vartheta \frac{\partial^2}{\partial \vartheta^2}\log g_t\right\} + \Sigma_r \bar{\mathrm{N}}_r \left\{\frac{\partial}{\partial \vartheta}\log \beta_r + \vartheta \frac{\partial^2}{\partial \vartheta^2}\log \beta_r\right\}\right] d\vartheta$$

$$+ \left[\Sigma_t \mathrm{X}_t \vartheta \frac{\partial^2}{\partial \vartheta \partial y_1}\log g_t + \Sigma_r \bar{\mathrm{N}}_r \vartheta \frac{\partial^2}{\partial \vartheta \partial y_1}\log \beta^r\right] dy_1 + \ldots$$

$$+ \Sigma_r \left[\vartheta \frac{\partial}{\partial \vartheta}\log \beta_r\right] d\bar{\mathrm{N}}_r.$$

Then

$$d\mathrm{Q} = \frac{1}{\log 1/\vartheta}\left[\Sigma_t \mathrm{X}_t d\left\{\log g_t + \log 1/\vartheta \,.\, \vartheta \frac{\partial}{\partial \vartheta}\log g_t\right\} + \Sigma_r \bar{\mathrm{N}}_r d\left\{\log \beta_r + \log 1/\vartheta \,.\, \vartheta \frac{\partial}{\partial \vartheta}\log \beta_r\right\} + \Sigma_r \left(\log 1/\vartheta \,.\, \vartheta \frac{\partial}{\partial \vartheta}\log \beta_r\right) d\bar{\mathrm{N}}_r\right],$$

$$= \frac{1}{\log 1/\vartheta}\left[d\,\Sigma_t \mathrm{X}_t \left(\log g_t + \log 1/\vartheta \,.\, \vartheta \frac{\partial}{\partial \vartheta}\log g_t\right) + d\Sigma_r \bar{\mathrm{N}}_r \left(\log \beta_r + \log 1/\vartheta \,.\, \vartheta \frac{\partial}{\partial \vartheta}\log \beta_r\right) - \Sigma_r \log \beta_r d\bar{\mathrm{N}}_r\right].$$

But by (2·3)

$$\log \beta_r = \log \bar{\mathrm{N}}_r - \Sigma_t q_{tr} \log \bar{\mathrm{M}}_t.$$

Therefore

$$\Sigma_r \log \beta_r d\bar{\mathrm{N}}_r = \Sigma_r \log \bar{\mathrm{N}}_r d\bar{\mathrm{N}}_r - \Sigma_t \log \bar{\mathrm{M}}_t (\Sigma_r q_{tr} d\bar{\mathrm{N}}_r),$$

$$= \Sigma_r \log \bar{\mathrm{N}}_r d\bar{\mathrm{N}}_r + \Sigma_t \log \bar{\mathrm{M}}_t d\bar{\mathrm{M}}_t,$$

with the help of (2·23). Thus this term is also a perfect

differential, and $(\log 1/\vartheta)dQ$ is a perfect differential. There exists, therefore, a function S of the equilibrium state of the assembly, called the entropy, and a function T of ϑ called the absolute temperature, which are such that $dQ = TdS$ if

$$\log 1/\vartheta = 1/kT, \quad . \quad . \quad . \quad . \quad . \quad (3{\cdot}2)$$

$$(S-S_0)/k = \Sigma_t X_t \left(\log g_t + \log 1/\vartheta \,.\, \vartheta \frac{\partial}{\partial \vartheta} \log g_t\right)$$

$$+\Sigma_r \overline{N}_r \left(\log \beta_r + \log 1/\vartheta \,.\, \vartheta \frac{\partial}{\partial \vartheta} \log \beta_r\right)$$

$$-\Sigma_r(\overline{N}_r \log \overline{N}_r - \overline{N}_r) - \Sigma_t(M_t \log \overline{M}_t - \overline{M}_t). \quad (3{\cdot}3)$$

The integration constant S_0 must be independent of any parameter in (3·2) which can change in the assembly. That is, S_0 is independent of ϑ, N_r, M_t, y_1, y_2, ..., but it can depend in any manner on the X's. Except for S_0 and the proportionality factor k, S and T are thus uniquely determined, and the identification of ϑ and $e^{-1/kT}$ is made with the full generality which is only possible by such an appeal to the *form* of the second law of Thermodynamics.

We can put (3·3) into a slightly different form by eliminating the X's with the help of (2·23). It then becomes

$$(S-S_0)/k = \Sigma_t M_t \left(\log \frac{g_t}{M_t} + 1 + \log 1/\vartheta \,.\, \vartheta \frac{\partial}{\partial \vartheta} \log g_t\right)$$

$$+\Sigma_r \overline{N}_r \left(\log \frac{h_r b_r}{\overline{N}_r \sigma_r} + 1 + \log 1/\vartheta \,.\, \vartheta \frac{\partial}{\partial \vartheta} \log \frac{h_r b_r}{\sigma_r}\right), \quad . \quad . \quad . \quad (3{\cdot}4)$$

$$= \Sigma_t \overline{M}_t \left(\log \frac{g_t}{\overline{M}_t} + 1\right) + \Sigma_r \overline{N}_r \left(\log \frac{h_r b_r}{\overline{N}_r \sigma_r} + 1\right)$$

$$+(E + \Sigma_r \overline{N}_r \chi_r) \log 1/\vartheta. \quad (3{\cdot}41)$$

The expected terms in ϑ^{χ_r} in (3·4) cancel.

For the vapour of a solid (crystal) in equilibrium with the solid, similar considerations apply. If we assume for simplicity that the external fields of force affect only the vapour molecules, we find at once by arguments similar to those above that

$$dQ = \frac{1}{\log 1/\vartheta} \left\{ X d\left(\log K + \log 1/\vartheta \,.\, \vartheta \frac{\partial}{\partial \vartheta} \log K\right) \right.$$

$$\left. + d\left(\overline{N} + \log 1/\vartheta \,.\, \vartheta \frac{\partial \overline{N}}{\partial \vartheta}\right)\right\}.$$

There exists, therefore, the required function S, given by

$$(S-S_0)/k = X \log K(\vartheta) + \overline{N} + E \log 1/\vartheta. \quad . \quad (3{\cdot}5)$$

This can be put into a form analogous to (3·4) with the help of (2·53). We obtain

$$(S-S_0)/k = (X-\overline{N})\left\{ \log K(\vartheta) + \log 1/\vartheta \,.\, \vartheta \frac{\partial}{\partial \vartheta} \log K(\vartheta) \right\} + N\left\{ \log \frac{h(\vartheta)\, b(\vartheta)}{N\sigma} + 1 + \log 1/\vartheta \,.\, \vartheta \frac{\partial}{\partial \vartheta} \log \frac{h(\vartheta)\, b(\vartheta)}{\sigma} \right\} \quad . \quad . \quad . \quad (3{\cdot}51)$$

$$= (X-\overline{N}) \log K(\vartheta) + \overline{N}\left(\log \frac{h(\vartheta)\, b(\vartheta)}{\overline{N}\sigma} + 1 \right) + (E - N\chi) \log 1/\vartheta. \quad (3{\cdot}52)$$

The analogy between (3·4) and (3·51) is now complete since $X-\overline{N}$ is the number of molecules in the crystal and χ is defined in opposite senses in the two cases.

We can now, by comparison of (3·4) and (3·51), see that each particular constituent makes a definite independent contribution to the entropy. The contribution of the body of gaseous molecules of type r is in both cases

$$N_r k \left[\log \left\{ \frac{h_r(\vartheta)\, b_r(\vartheta)}{N_r \sigma_r} \right\} + 1 + \log 1/\vartheta \,.\, \vartheta \frac{\partial}{\partial \vartheta} \log \left\{ \frac{h_r(\vartheta)\, b_r(\vartheta)}{\sigma_r} \right\} \right]. \quad . \quad . \quad . \quad (3{\cdot}6)$$

The contribution of a crystal of M molecules is

$$Mk \left[\log K(\vartheta) + \log 1/\vartheta \,.\, \vartheta \frac{\partial}{\partial \vartheta} \log K(\vartheta) \right]. \quad . \quad (3{\cdot}61)$$

The entropy of the whole assembly of which these may be constituent parts contains an indeterminate constant, but this constant cannot depend on any parameter appearing in (3·6) or (3·61). The formal dependence of these expressions on the number of systems (N, M) is now fully specified, because we have considered systems in which the numbers of constituents can be reversibly changed *.

It is further clear that the molecules of type r make the contribution (3·6) to the entropy of any assembly in statistical equilibrium in which there are N_r molecules in a volume V at temperature ϑ. If we think of such an assembly in which the possibility of dissociation is

* Ehrenfest and Trkal, *loc. cit.* p. 163.

temporarily suspended, so that the assembly is in statistical equilibrium with the N's and M's fixed, the contribution to the entropy made by the rth type of molecule can be regarded as still given by (3·6).

In addition to the unspecified constant in the entropy of the whole assembly, the entropy contributions of the various species are not quite as absolute as they appear to be, for they depend on the precise convention by which unit weight is assigned. That is to say, they really contain an unspecified multiple of M or N. A change in this convention will change the values of the entropy contributions, but in such a way as to make no difference to any physical result. Whether or no we admit the idea of absolute entropy, these formulæ for the entropy contributions which we have just obtained are all that can be required in actual argument.

§ 4. *Use of the characteristic function.*—As we have already shown for non-dissociating assemblies, the connexion between thermodynamics and statistical mechanics can be simplified by the use of Planck's Characteristic Function Ψ as the primary thermodynamic quantity. Ψ is defined in thermodynamics by the equation $\Psi=S-E/T$, and has the properties

$$E = T^2\frac{\partial\Psi}{\partial T}, \quad S = \Psi+T\frac{\partial\Psi}{\partial T}, \quad Y_1 = T\frac{\partial\Psi}{\partial y_1}. \quad . \quad (4\cdot1)$$

In order to make Ψ fundamental, we recall the integral for C (2·24), and it is evident that we have only to define Ψ in such a way that

$$C = \frac{1}{2\pi i}\int_\gamma \frac{dz}{z^{E+1}}e^{\Psi(z)/k}; \quad . \quad . \quad . \quad . \quad (4\cdot2)$$

the thermodynamic theorems follow at once.

To make a simple definition, we use the fact that all the details of the distribution laws for the assembly, including to a sufficient approximation the value of C, are the same as if the M's and N's are fixed at their equilibrium values. The number of such examples of the assembly is

$$\frac{X_1!\ldots X_s!}{\overline{M}_1!\ldots\overline{M}_s!\ \overline{N}_1!\ldots\overline{N}_j!\ \sigma_1^{\overline{N}_1}\ldots\sigma_j^{\overline{N}_j}}.$$

Definition. *The characteristic function of an assembly is k times the sum of the logarithms of the partition functions of all the component systems in the assembly plus the logarithm*

of the number of possible examples of the assembly, when the numbers of the various systems have their equilibrium values and the argument of the partition functions is $\vartheta = e^{-1/kT}$.

It is not conveniently possible to avoid making the identification of ϑ and $e^{-1/kT}$ part of the definition. No attempt to use the first equation in (4·1) as a means of connecting ϑ and T, on the assumption that we know E and Ψ as functions of ϑ, can possibly succeed in making T precise—a difficulty pointed out in § 6 of the second paper.

According to these definitions, we find for the two types of assembly we are discussing :

$$(\Psi-\Psi_0)/k = \Sigma_t \mathrm{M}_t\left(\log\frac{g_t}{\mathrm{M}_t}+1\right)+\Sigma_r\bar{\mathrm{N}}_r\left(\log\frac{h_r b_r}{\bar{\mathrm{N}}_r\sigma_r\vartheta^{\chi_r}}+1\right), \quad . \quad . \quad . \quad (4\cdot3)$$

$$(\Psi-\Psi_0)/k = \mathrm{X}\log\mathrm{K}(\vartheta)+\bar{\mathrm{N}}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4\cdot4)$$

$$= (\mathrm{X}-\bar{\mathrm{N}})\log\mathrm{K}(\vartheta)+\bar{\mathrm{N}}\left(\log\frac{hb}{\mathrm{N}\sigma\vartheta^{-\chi}}+1\right). \quad (4\cdot41)$$

These definitions actually determine the value of the constants Ψ_0, and therewith S_0, for $\Psi_0=\mathrm{S}_0$, though the values of these constants are immaterial. In fact, with sufficient accuracy,

$$\Psi_0/k = \Sigma_t(\mathrm{X}_t\log\mathrm{X}_t-\mathrm{X}_t)$$

in (4·3), (4·4), or (4·41).

§ 5. *The usual introduction of entropy into statistical mechanics and the "increasing property" of entropy.*—In ordinary presentations of entropy in statistical mechanics the property of entropy which is taken as fundamental is its "increasing property." This presentation has already been critically considered*, but we can now push the analysis somewhat further.

Properly enunciated, the postulate of the increasing property is equivalent to some such statement as the following :—

(1) If an assembly in statistical equilibrium is divided into two parts by some such workless process as the closing of an ideal door, the sum of the entropies $\mathrm{S}_1+\mathrm{S}_2$ for the two parts after separation is equal to the entropy S_{12} of the whole before separation.

(2) If two assemblies separately in equilibrium are joined together into one assembly in a similar way, the joint

* Second paper, § 4.

assembly takes up a new equilibrium in which $S_{12} \geq S_1 + S_2$, equality being only possible under certain special conditions of equal temperatures and concentrations.

It has already been shown for less general assemblies * that no introduction of entropy on the basis of this postulate can lead without ambiguity to the absolute temperature scale. These arguments are equally valid here in the general case. It was shown further that the least objectionable definition of entropy from this standpoint is a definition of "kinetic entropy" as k times the logarithm of the number of weighted complexions representing the specified state of the assembly. Kinetic entropy is a fluctuating quantity. If, as usual, a non-fluctuating quantity is required, it was shown that we may best define the "statistical entropy" as k times the logarithm of the total, average, or maximum number of weighted complexions. These numbers are indistinguishable from each other and from $k \log \Omega$. In the previous case such a definition is reasonably satisfactory, as it provides naturally a function S which has the desired increasing property for simple cases of junction, in which the separate assemblies can after junction exchange energy only, so that only their temperature can change. This S does in fact agree with the entropy of thermodynamics so long as the number of systems in a group does not change. Junctions resulting in changes of volume, for example, were not considered. For such junctions the function $k \log \Omega$ as defined in the simple case does not possess the required increasing property.

To discuss general cases of junction, we must be prepared to allow changes in the number of systems in a group. Such changes can take place in a dissociating assembly, and a definition should therefore now be possible on these lines. If, as before, we take $k \log \Omega$ for the statistical entropy, we obtain an expression which agrees with (3·41) in its variable part and assigns to S_0 the value Ψ_0 of § 4. We shall show in the next section that the variable part of S does now in fact possess the increasing property in all circumstances, but it is obvious that the complete $k \log \Omega$ does not. It follows that $k \log \Omega$, *if we drop the constant term*, is a suitable definition for S. But the need to eliminate this constant term means that there is now no entirely natural definition of this sort which can at once be shown to possess the increasing property.

* Second paper, § 6.

It is now well to consider somewhat more closely the implications of postulating the increasing property as the fundamental property of entropy. It implies in particular that the entropy of two gram-molecules of a gas X must be twice that of one gram-molecule at the same temperature and concentration. This is as it should be (in agreement with § 3) when the two gram-molecules or one gram-molecule are both parts of the same assembly in which the amount of X present can be reversibly changed. But the postulate asserts it in all cases, and asserts in general that entropies must be directly comparable whether or not they correspond to states which can be connected by a reversible process. There is no need whatever that this should be so. In asserting it, we are actually going a long way towards asserting the existence of *absolute entropy* and making a special choice of the constant S_0 for the assembly and each of its parts. It is not therefore surprising that there is no natural method of defining S, constant and all, in such a way that the increasing property is satisfied.

If we accept the position that the constant terms in the entropy are meaningless and need not satisfy the increasing property, then $k \log C$ retains its suitability for a definition of statistical entropy. We have already seen that it agrees with S as introduced by the classical method of § 3. But $k \log C$ has of course the usual wider range of validity in that it applies to and defines the entropy for statistical states of the assembly which are in no sense equilibrium states. It is perhaps chiefly to obtain this generalization of entropy that entropy has been introduced so often into statistical mechanics, as k times the logarithm of the "thermodynamic probability." The increasing property has been used as the simplest way of making this introduction plausible, and (probably) not from any real sense of its more fundamental character. When this generalization is required, my own attitude is that entropy is best defined outright as $k \log C$ and justified by comparison with S introduced as in § 3.

Whether we prefer to take the increasing property as fundamental or as a deduction, the fact that, suitably defined, the entropy possesses it is interesting and important. We give the necessary proofs in the next section.

§ 6. *Proof of the increasing property.*—It is simplest to discuss the problem of junction in two stages. Consider a dissociating assembly in equilibrium, for which the external

forces represent only the retaining walls of the enclosure containing it. With $S_0=0$, the entropy is given by

$$S_1/k = \Sigma_t M_1\left(\log\frac{g_1}{M_1}+1\right)+\Sigma_r N_1\left(\log\frac{h_1 b_r}{N_1\sigma_r}+1\right) + (E_1+\Sigma_r N_1\chi_r)\log 1/\vartheta_1, \quad (6{\cdot}1)$$

and the temperature ϑ_1 is given in terms of E_1 by an equation equivalent to $\partial S_1/\partial\vartheta_1=0$. For convenience the suffixes t and r are temporarily omitted in the M's, N's, g's, and h's which require a suffix 1 or 2 to distinguish the two assemblies, and the bars are dropped. A similar expression gives the entropy of the second assembly. When the assemblies are joined, the M's and N's will in general change. It will not affect, however, the final inequality if we suppose to start with that on junction all the M's and N's remain fixed. For such an assembly we can calculate an intermediate function * s_{12}, which has the same form as S_{12} with the artificial values of the M's and N's. This is the first stage. In the second stage we suppose the M's and N's to change to their equilibrium values when the entropy is S_{12}.

At the end of the first stage we have therefore

$$s_{12}/k = \Sigma_t(M_1+M_2)\left(\log\frac{g_{12}}{M_1+M_2}+1\right) + \Sigma_r(N_1+N_2)\left(\log\frac{h_{12}b}{(N_1+N_2)\sigma_r}+1\right) + [(E_1+E_2+\Sigma_r(N_1+N_2)\chi_r]\log 1/\vartheta_{12}. \quad (6{\cdot}11)$$

In this equation we are to suppose, as is always possible, that ϑ_{12} is determined in terms of E_1+E_2 by the standard equation (2·41), which is equivalent to

$$\partial s_{12}/\partial\vartheta_{12}=0. \quad . \quad . \quad . \quad . \quad . \quad (6{\cdot}12)$$

Consider the value of $(s_{12}-S_1-S_2)/k$, taking separately the terms dependent on the volumes † V_1, V_2, and V_{12}, and on ϑ_1, ϑ_2, and ϑ_{12}. The volume terms consist of a set of terms of the form

$$f=(M_1+M_2)\log\frac{V_1+V_2}{M_1+M_2}-M_1\log\frac{V_1}{M_1}-M_2\log\frac{V_2}{M_2}. \quad (6{\cdot}2)$$

* If we accept a definition based on $k\log C$ for the entropy, then s_{12} is itself the entropy, and the statement of the proofs of this section can be slightly simplified.

† There is no reason to suppose that the volumes are the same for all different molecular species in the two assemblies. So far as different volumes can be obtained by semi-permeable membranes, they can be supposed to occur in these formulæ. Thus $(g_t)_1$ contains the factor $(V_t)_1$ etc.

Now $f=0$ when $M_1/V_1=M_2/V_2$, and

$$\frac{\partial f}{\partial M_1}=\log\frac{V_1+V_2}{M_1+M_2}-\log\frac{V_1}{M_1};$$

so that $\partial f/\partial M_1=0$ when $M_1/V_1=M_2/V_2$. Finally

$$\frac{\partial^2 f}{\partial M_1^{\,2}}=-\frac{1}{M_1+M_2}+\frac{1}{M_1}\geq 0.$$

Thus in all cases $f\geq 0$, and equality can only hold when $M_1/V_1=M_2/V_2$. The argument applies to each term of the set.

Consider next the ϑ-terms. These are of exactly the same form as in the simple case of non-dissociating assemblies, and the argument of the former paper applies. It follows therefore that

$$s_{12}\geq S_1+S_2$$

in all cases, and that the equality can hold if and only if

$$(M_t/V_t)_1=(M_t/V_t)_2,\quad (t=1,\ldots,s), \qquad (6{\cdot}31)$$

$$(N_r/V_r)_1=(N_r/V_r)_2,\quad (r=1,\ldots,j), \qquad (6{\cdot}32)$$

$$\vartheta_1=\vartheta_2. \qquad (6{\cdot}33)$$

If (6·31), (6·32), and (6·33) are all satisfied, then

$$\vartheta_1=\vartheta_2=\vartheta_{12}.$$

In the second stage we have a single assembly, for which we can drop the suffixes 1, 2, and a function s of the state of that assembly which is given by the same formula as S for the final equilibrium state. The only difference is that in general the values of the M's and N's are not the equilibrium values. As the M's and N's change subject to (2·23), ϑ will also change subject throughout to (6·12). Thus

$$\frac{ds}{dN_r}=\frac{\partial s}{\partial N_r}+\Sigma_t\frac{\partial s}{\partial M_t}\frac{\partial M_t}{\partial N_r}+\frac{\partial s}{\partial\vartheta}\frac{\partial\vartheta}{\partial N_r}=\frac{\partial s}{\partial N_r}+\Sigma_t\frac{\partial s}{\partial M_t}\frac{\partial M_t}{\partial N_r}$$

$$=\log\frac{\beta_r M_1^{\,q_{1r}}\ldots M^{\,q_{sr}}}{N_r}. \qquad (6{\cdot}4)$$

When the N's have their correct equilibrium values,

$ds/d\mathrm{N}_r=0$. Further,

$$\frac{d^2s}{d\mathrm{N}_r^2}=-\frac{1}{\mathrm{N}_r}-\Sigma_t\frac{q_{tr}^2}{\mathrm{M}_t}+\frac{\partial}{\partial\vartheta}\log\beta_r\frac{\partial\vartheta}{\partial\mathrm{N}_r},$$

$$=-\frac{1}{\mathrm{N}_r}-\Sigma_t\frac{q_{tr}^2}{\mathrm{M}_t}-\frac{\left(\vartheta\dfrac{\partial}{\partial\vartheta}\log\beta_r\right)^2}{\vartheta\,\partial\mathrm{E}/\partial\vartheta}<0\,;$$

$$\frac{d^2s}{d\mathrm{N}_r d\mathrm{N}_{r'}}=-\Sigma_t\frac{q_{tr}q_{tr'}}{\mathrm{M}_t}-\frac{\left(\vartheta\dfrac{\partial}{\partial\vartheta}\log\beta_r\right)\left(\vartheta\dfrac{\partial}{\partial\vartheta}\log\beta_{r'}\right)}{\vartheta\,\partial\mathrm{E}/\partial\vartheta}.$$

It easily follows that the second-order terms in an expansion of s in the neighbourhood of its correct equilibrium value S can be expressed as a set of square terms all with negative coefficients, and that therefore $s-\mathrm{S}$ is essentially negative. The second stage can therefore only result in a further increase of S_{12} over $\mathrm{S}_1+\mathrm{S}_2$.

We have therefore established, with a suitable definition of S, the relation

$$\mathrm{S}_{12}\geq\mathrm{S}_1+\mathrm{S}_2.$$

It remains only to show that the conditions (6·31), (6·32), and (6·33) are sufficient for actual equality, and for this it is only necessary to show that under these conditions the changes of the second stage are nil. The conditions that determine the M's and N's in any assembly, written in full, are

$$\frac{\mathrm{M}_1^{q_{1r}}\ldots\mathrm{M}_s^{q_{sr}}}{\{g_1(\vartheta)\}^{q_{1r}}\ldots\{g_s(\vartheta)\}^{q_{sr}}}=\frac{\mathrm{N}_r\sigma_r\vartheta^{\chi_r}}{h_r(\vartheta)b_r(\vartheta)},\quad\ldots\quad(6\cdot5)$$

and for any value of r and t

$$g_t(\vartheta)=\mathrm{V}_t\mathrm{G}_t(\vartheta),\quad h_r(\vartheta)=\mathrm{V}_r\mathrm{H}_r(\vartheta),$$

where in $\mathrm{G}_t(\vartheta)$ and $\mathrm{H}_r(\vartheta)$ ϑ is the sole variable. If, therefore, (6·5) is satisfied for the separate assemblies before junction, and the conditions (6·31), (6·32), and (6·33) are satisfied, (6·5) will still be satisfied for the complete assembly after junction, which will therefore be in its equilibrium state without further change. The second process therefore vanishes, and we have the equality

$$\mathrm{S}_{12}=\mathrm{S}_1+\mathrm{S}_2.\quad\ldots\quad(6\cdot6)$$

These conditions are therefore both necessary and sufficient.

If we carry out the converse process and divide the

assembly into two separate parts, the same conditions will be automatically satisfied, ignoring fluctuations, and so the equality (6·6) is necessarily valid. The deduction of the increasing property of S for assemblies in statistical equilibrium is thus completed.

An exactly similar proof holds for the entropy of the vapour-solid combination in equilibrium.

§ 7. *Nernst's Heat Theorem and the Chemical Constants.*—Nernst's Heat Theorem may be enunciated in the following form:—*In a "condensed system" the change of entropy in any isothermal reversible process tends to zero as the temperature tends to zero.* For any "condensed system" for which we can construct the partition function we can examine the position of Nernst's Theorem in statistical theory. Suppose first that the partition function for one molecule before and after the reaction has respectively the simple form

$$\Sigma_r p_r \vartheta^{\epsilon_r}, \quad \Sigma_r q_r \vartheta^{\eta_r}.$$

All the degrees of freedom are thus thought of as of one type, and their total number can never be changed by any reaction. Now the contribution to the entropy of the assembly made up of N molecules of the substance in either form is

$$Nk\left[\log f(\vartheta) + \log 1/\vartheta \,.\, \vartheta \frac{\partial}{\partial \vartheta} \log f(\vartheta)\right],$$

where f is the partition function. As $\vartheta \to 0$, this tends to

$$Nk\left[\log p_0 \vartheta^{\epsilon_0} + \log 1/\vartheta \,.\, \vartheta \frac{\partial}{\partial \vartheta} \log p_0 \vartheta^{\epsilon_0}\right] = Nk \log p_0$$

before the reaction, or $Nk \log q_0$ after the reaction. Thus Nernst's Theorem is equivalent to the statement that *the weights of the lowest quantum states must be equal* *. If, and only if, this is the case, then Nernst's Theorem follows at once as a direct consequence of statistical theory. There is no need for any appeal to the conception of *absolute* entropy.

The simple case examined above hardly corresponds to actual facts. An important real case which we can examine is that of a reaction between solids in the crystalline form †.

* This result was pointed out in a preliminary way in the Second paper, § 8.

† The actual reaction may, if necessary, be supposed to take place in a vapour phase present in negligible quantity in the assembly.

The contribution to the entropy of the assembly of any crystal containing any molecules is

$$Nk\left[\log \mathrm{K}(\vartheta)+\log 1/\vartheta \,.\, \vartheta\frac{\partial}{\partial\vartheta}\log \mathrm{K}(\vartheta)\right].$$

It can be shown * that Born's † results on the mean energy of a crystal can be translated at once into results on partition functions. If we ignore the possible ultra-violet absorption frequencies of the crystal due to the motion of the electrons ‡ as distinct from the complete atoms, we find

$$\log \mathrm{K}(\vartheta) = -\frac{3}{(\log 1/\vartheta)^3}\sum_{j=1}^{3}\frac{1}{k^3\Theta_j{}^3}\int_0^{k\Theta_j \log 1/\vartheta} x^2 \log\,(1-e^{-x})\,dx - \sum_{j=4}^{3(n-1)} \log\,(1-\vartheta^{h\nu_j}), \quad . \quad . \quad . \quad (7{\cdot}1)$$

where n is the number of atoms in an elementary cell of the crystal lattice, and the Θ_j, ν_j are constants characteristic of the crystal. We must interpret the molecule in the crystalline state for the purposes of this formula as the collection of all the atoms in one elementary cell.

When $\vartheta \to 0$,

$$k\Theta_j \log 1/\vartheta \to \infty,$$

and

$$\int_0^{k\Theta_j \log 1/\vartheta} \to \int_0^{\infty} x^2 \log\,(1-e^{-x})\,dx = 2\sum_1^{\infty}\frac{1}{n^4} = \frac{\pi^4}{45}.$$

The second set of terms all tend to zero like a power of ϑ, and thus except for a constant multiple $\log \mathrm{K}(\vartheta)$ behaves like

$$\frac{1}{(\log 1/\vartheta)^3}.$$

Both terms in the entropy therefore tend to zero as $\vartheta \to 0$, and as the entropy contributions all vanish, their difference vanishes and Nernst's Heat Theorem holds for all such reactions.

It is important, however, to look somewhat more closely into this result. Formula (7·1), on which it depends, is based on the usual analysis into normal coordinates of the motion of a dynamical system executing small vibrations.

* Darwin and Fowler, Proc. Camb. Phil. Soc. *loc. cit.*

† 'Der Dynamik der Krystallgitter,' Chap. 5.

‡ It is correct to do so here, for we consider the atoms as the structural units in this discussion. The internal mechanism and construction of the atoms we must ignore consistently throughout.

Each such coordinate is treated like Planck's line vibrator, and its lowest quantum state (of zero energy) is assigned the weight unity. The result, however, cannot and does not depend on this convention. If we assign the weight p_0 to such a state, keeping of course relative weights unaltered, the expression (7·1) for $\log K(\vartheta)$ will be altered by the addition of the term

$$3n \log p_0.$$

The entropy is altered by the addition of the term

$$3Nn \log p_0, \quad . \quad . \quad . \quad . \quad . \quad . \quad (7{\cdot}2)$$

where Nn is the number of atoms in the crystal, and (7·2) is now the limit of the entropy as $\vartheta \to 0$. This does not in any way affect the vanishing of the entropy *change* as $\vartheta \to 0$, for, as the total number of atoms cannot alter, the same constant limit must occur in both the values of the entropy before and after the reaction *.

Nernst's Heat Theorem for reactions between crystals is therefore, on the general principles of the quantum theory, a deduction from the fact that the weights of the lowest quantum states of such systems are necessarily equal. This equality is a result of the form into which the internal motions of the crystals can be analysed. It is not yet possible to establish fully the validity of the theorem on the same basis for other types of condensed systems—liquids and supercooled liquids (glasses)—in the absence of suitable partition functions. It is, however, not unreasonable to suppose that its truth ultimately rests on the same analysis of the internal motion into normal modes and the same consequent equality of the weights of the lowest quantum states.

A particular use of Nernst's Theorem is to deduce the form of dissociation-equilibria in gases, from the vapour-pressure equation of each gas, showing in particular that the constant in the equation of dissociation-equilibrium can be expressed in terms of the constants in the vapour-pressure equations, the so-called chemical constants. It is, in fact, on account of this property that the chemical constants earn their name. It has been shown in the third paper † that this property can be most naturally

* It is presumably not even necessary to assign the same weight to the lowest quantum state of different kinds of atoms executing simple harmonic vibrations. The weights for any one kind of atom must of course be the same in all crystals. But I have not examined this point in detail.

† In generalization of a similar theorem due to Ehrenfest and Trkal, *loc. cit.*

established directly as a theorem in statistical mechanics without appeal to Nernst's Theorem. It is now clear that both this property and Nernst's Theorem itself are consequences of the same facts: namely, the particular behaviour of the partition function for any crystal, and probably for other solids and liquids as well, as $T \rightarrow 0$.

Summary.—Finally, one may perhaps briefly re-state the central idea of the series of papers here concluded. We have approached the subject of statistical equilibrium from the standpoint that its characteristics are determined by the *average* values of certain quantities taken over all dynamically possible states of an assembly—all states, that is to say, with the given total energy. It has been found possible to work out the details of the equilibria in fairly general cases without any appeal to thermodynamical ideas. The position is maintained that such ideas are really irrelevant in statistical theory except for the logical introduction of the absolute temperature, and the ordinary introduction of entropy into statistical theory is criticized. At the same time the fact that the laws of thermodynamics are deductions from the theory is important, and has been established for all the assemblies discussed.

LIV. *Electrical Properties of a Flint Glass of Density* 6·01. *By* G. L. Addenbrooke *.

IN a Royal Society paper (Phil. Trans., 1878) Hopkinson described measurements of the specific inductive capacities or dielectric constants of four kinds of Flint Glass of increasing densities, which have since been quoted in tables of constants.

He ends his paper as follows :—

"If the electrostatic capacities (K) be divided by the density (D) we find the following quotients :—

	D.	K.	$\frac{K}{D}$.	Refractive index D line.
Very light Flint ...	2·87	6·57	2·29	1·541
Light Flint	3·2	6·85	2·14	1·574
Dense Flint	3·66	7·4	2·02	1·622
Double extra dense..	4·5	(10·1)	(2·25)	1·710
		(9·98)	(2·22)	

* Communicated by the Author.

"Thus $\frac{K}{D}$ is not vastly different from a constant quantity.

"Messrs. Gibson and Barclay find for paraffin 1·977: taking the density of paraffin as 0·93, we have the quotient of 2·13. This empirical result cannot of course be generally true, or the capacity of a substance of small density would be less than unity."

Dielectric Constants of Heavier Glasses.

The glass of the greatest density examined by Hopkinson was 4·5. In 1909, Thornton made measurements on an ellipsoid of glass of density 4·65 (Proc. Royal Soc., 1909). The dielectric constant of this he gives as 10.64. In his paper he puts Hopkinson's and his own results in the form of a curve, which is reproduced and extended below..

Shortly after the publication of Thornton's paper, Messrs. Hilger informed me that there was a glass of 4·85 density obtainable, from which they could cut a thin sheet 6 inches square. I obtained such a sheet and measured its dielectric constant, in 1911, by an alternating-current method, comparing it with a standard air-condenser. The constant 11·2 was again higher and fitted in with a prolongation of Thornton's curve. Unfortunately it was broken before the final corrections could be made. At the same time I found that at the Jena factory they made a glass of about 6 density. Messrs. Hilger, however, stated that they could not get this in a size from which they could cut a disk more than 4 inches in diameter.

I thought this too small at the time to get good results, having regard also to the risks of breakage and cost; but it occurred to me that a test might be made of the glass in the form of fragments by a method of mixture, and Messrs. Hilger were good enough to procure for me some lumps of the glass.

The particulars are as follows:—

Properties of Dense Silica Flint.

Refractive Index for D-line.	Medium disp. C–F line.	Density
1·9201	0·04381	6·01

Approximate Composition ..... SiO 22%; PbO, 78%.

The glass has a decidedly yellow tinge but otherwise is quite transparent. Exposed since in the laboratory for some ten years, the surface shows slight traces of action, but a little protection would evidently have obviated this.

Judging by its density and composition, the density of natural silica being 2·61, fused silica 2·0, and lead 19·2, it must contain ever 30 per cent. by volume of metallic lead. It breaks easily, though hard. It softens and melts at a fairly low red-heat without showing any signs of blackening. That such a composition should be perfectly transparent and a high-class insulator is remarkable enough in itself.

Other matters prevented me going further with this glass at the time, and the war coming on, it was not until lately that I was able to do more with it.

In the meantime I found that the method of mixture had been used by Thwing to obtain the dielectric constants of a number of substances in fragments or powder form and that his results were accepted by writers of works of reference (Physical Review, July–Aug. 1894). Thwing does not give any details beyond the formula, but as there are several points of importance which need attention to secure accuracy, a memorandum is here appended dealing with them. In view of the great improvements and facilities for measuring small capacities which have become available during the last few years, the method is readily workable and could be employed for the measurement of the electrical properties of a number of substances of which at present little is known.

As the result of several trials, the dielectric constant of the above glass of density 6 was finally found to be 13, within from 2 to 3 per cent.

So far as I am aware this is not only the highest dielectric constant yet found for any glass, but it is the highest found for any material not of abnormal character and not complicated by the effects of absorption. Apparently also, the glass in question is the substance for which the deviation from Maxwell's relation of the dielectric constant to the square of the refractive index is greatest, when uncomplicated by the effects of absorption.

The data are given below for the range of glasses :—

Relation of K to the Square of Refractive Index.

	(1)	(2)	(3)	(4)	(5)	(6)
Density.....	2·87	3·2	3·66	4·12	4·5	6·01
K	6·57	6·85	7·4	8·52	9·98	13·0
N^2.....	2·35	2·45	2·58	2·85	3·0	3·68
K/N^2.....	2·8	2·75	2·86	3·0	3·33	3·55

The specimen of glass of density 6 is not quite the densest known, there is another (see Smithsonian Tables, 1910, p. 180) of a density of 6·33. The composition of this is given as SiO_2 21·9 per cent., PbO 78 per cent., and traces of arsenic.

Now there is a definite chemical compound known as $PbSiO_3$. If a calculation is made of the respective weights of its components, it would appear to be composed of PbO 78·6 per cent. and SiO_2 21·4 per cent. Consequently, this densest glass corresponds with the chemical compound $PbSiO_3$ with a small fraction of silica dissolved or mixed in it, and the specimen under discussion with a density of 6 may consist essentially of this compound *plus* a fraction more silica.

Mr. Frink, the director of the Glass Research Association, informs me that with these very dense glasses the difficulty is to prevent this compound crystallizing out, and hence the great importance of stirring. He has given me a small specimen of this compound, and offered to try and obtain sufficient of it in a pure state to enable its electrical properties to be determined. A test on such a specimen would complete the investigation. It does not seem probable that its properties would differ appreciably from those of the glass of 6·33 density, the refractive index of which is 1 96.

All these glasses are essentially a mixture of silica and lead oxide. Since the constituents can form a definite compound, apparently this compound will be formed as far as the proportions admit, and then this compound is dissolved in the remaining free silica, or mechanically mixed with it, each aggregate probably retaining essentially its physical properties.

Note.—Since writing the above Mr. Frink has further pointed out to me that, if a specimen of heavy glass has crystallized out, and the crystals are examined with a good magnifying glass, it will be found that mixed with the usual form of the crystals there are a certain number of others, of the same order, but of a more elongated shape and with certain other slight differences, which point to there being present a second slightly different silicate of lead. It might therefore be that all the Silica is divided up between these two compounds.

Thus the glass of density 6 seems to be very near the limit of what can be done by mixture, so that we are near the end of a definite series, and its electrical and optical properties should closely approximate those of the definite chemical compound. It will be noted that the relation of K to N^2 continually increases. It may be that the final density of 6·33 which has been attained is due to a reduction of volume on crystallization, as natural quartz is denser than fused silica, rather than to a correspondingly higher proportion of lead.

Observations on Curves showing results for the Series of Flint Glasses.

Electrical Properties.

Having now dealt with these matters it is interesting to plot for the series of glasses Hopkinson's and Thornton's results with the new determination.

Mr. Dye, of the N. P. L., has also drawn my attention to a communication to the *Jahrbuch Zeitschrift für Drachtlose Telegraphie und Telephonie* for August 1921, in which E. Schott gives a new set of determinations of the dielectric constants of Jena glasses. The glass with the highest constant included in it is No. 198 *b*. Having a dielectric constant of 11·3 and refractive index 1·77, this is evidently the same glass of density slightly under 5 mentioned by me above for which I found a dielectric constant of about 11·2.

I understand that since the war there has been a difficulty in making the glass of 6 density which forms the subject of this communication, and that it is not at present procurable.

Three of Schott's results are inserted in the diagram. It will be seen that they agree well with Hopkinson's and Thornton's, and thus confirm them and the general character of the curve.

The left-hand curve in the diagram covers the relation of density to K or rather to (K − 1). (On this point see Addenbrooke, Faraday Soc. Proceedings, Dec. 1919.) The values of the (K − 1) of these glasses lie in a curve of which a line drawn from the densest—or what we may venture to take as approximating the (K − 1) of the chemical compound—seems to form the axis. This point I hope to show later has considerable significance.

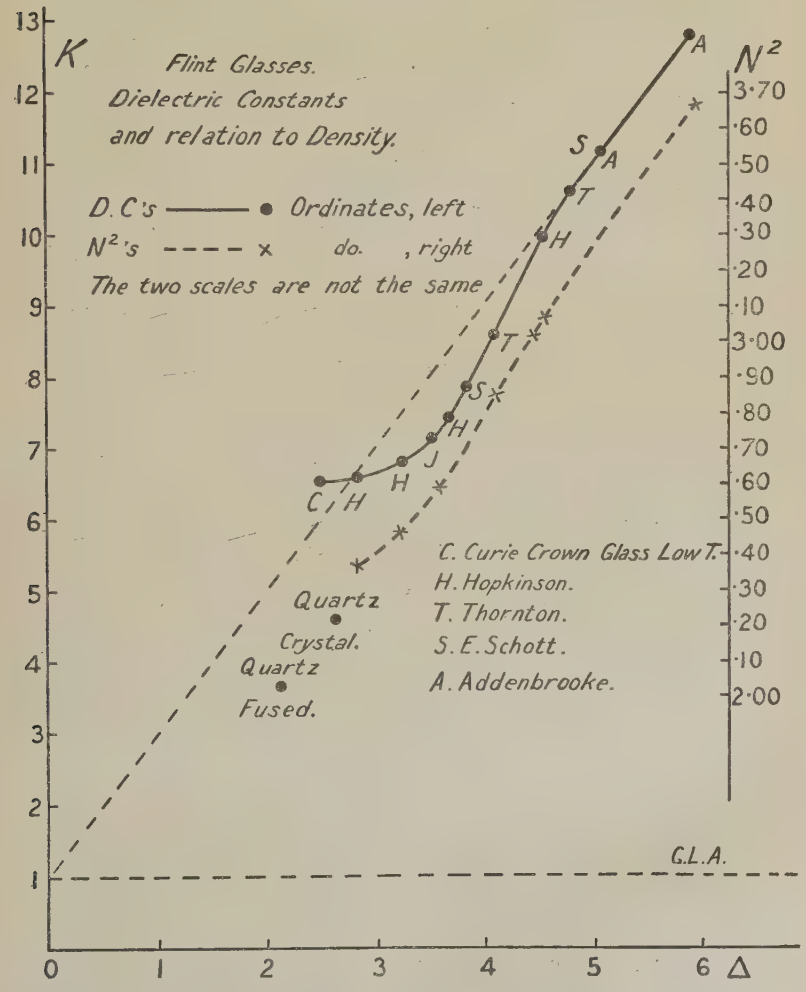
In considering the curves and data, as the electrical properties are volume properties, it is important to bear in mind the great differences in volume covered by different proportions in weight of the various constituents.

According to Pulfrich's analysis (French Physical Society Tables) all the glasses of lower density have either potash or soda in their composition, also possibly barium, but as the density increases they are more and more completely composed of lead oxide and silica. The composition of Hopkinson's glasses is unknown, but probably silica does not differ much from that of the Jena glasses.

The above analysis of the composition of these glasses is given in percentages of PbO and SiO_2. There appears to be some doubt amongst chemists as to how far these glasses are mixtures of these compounds or are increasingly $PbSiO_3$

plus SiO_2. From work on the relation of the dielectric constants of substances to their other physical properties the evidence seems to me strongly in favour of chemical combination, and also against the inference that either lead or

Fig. 1.



dissolved lead oxide has a specially high dielectric constant. The raising of the dielectric constant so high is the result of chemical combination. It would, however, take up too much space to give here the further evidence on which these views are formed.

Optical Properties.

In the above diagram with ordinates on the right side, there is given for comparison a curve of the squares of the refractive indices for these glasses. It will be seen that the inflexion of the lower part of the curve is also shown in this, though naturally to a less degree, and on a different scale.

Details of the methods by which the above results were obtained are appended below.

The method of obtaining Dielectric Constants of Substances in Mixture.

The method consists in forming an air-condenser with metal electrodes of known area, say 250 sq. cm. spaced, say, 2 to 5 mm. apart. This air-condenser, being in the form of a box with open top, can be filled with granules or powder of any material to be investigated.

If the density of the material is known, the volume which fills the container can be found by adding previously weighed portions, and no filling with a second substance is necessary.

If, however, the density of the substance is not known or it is desired for other purposes not to expose the material to the air, then a second liquid substance is added. In most cases, ordinary paraffin oil which has been dried by shaking up with powdered calcium carbide is convenient, and its dielectric constant can be taken as very close to 2.

From its dimensions we know the volume and area of the container.

The true air capacity of the condenser between electrodes is found from the dimensions, but as the thickness is small it is advisable to correct this by a calculation of the volume and area. The volume can be obtained very closely by first filling the container with liquid, say petrol, and then measuring the volume, after which the container can be dried before putting in the granules or powder.

The container is then filled with granules or powder. Paraffin oil is put in a litre measure-glass and its volume carefully noted. Oil is now poured into the container until it is full, after shaking to get rid of bubbles. The difference in the measure-glass gives the volume of oil needed ; as an extra precaution the container may be put under a receiver and exhausted of air. Then

$$\text{Vol. container} - \text{vol. oil} = \text{vol. solid.}$$

I have mentioned the true air capacity of the condenser because much turns on this. It is insufficient to trust to

calculation alone. A careful electric measurement of the capacity of the condenser when empty must first be made in the position in which it is to be finally used; this of course includes all stray and other lines which do not pass directly between the electrodes, and this correction will be found very considerable : this is the chief point requiring special attention to secure accuracy.

We then have :

$$\text{Outside cap. of condenser} = \text{Measured air cap. of condenser} - \text{Calculated air capacity}$$

then

$$\text{True cap. of mixture} = \text{Measured cap. of mixture} - \text{Outside cap. of condenser}$$

and

$$\text{K of mixture} = \frac{\text{True cap. of mixture}}{\text{Calculated air cap. of condenser}} ;$$

and this is the value of K, which should be used in Thwing's formula

$$\text{K solid} = \frac{(\text{Vol. mix.} \times \text{K mix.})(\text{Vol. liq.} \times \text{K liq.})}{\text{Vol. solid}} .$$

The condenser or container was formed as follows :—

Two flat sheets of plate-glass and a length of square rubber cord of 5 mm. section were taken. The rubber cord, cut nearly through at the corners, was fixed to one sheet of glass with strong rubber solution so as to enclose an area, say, of 250 sq. cms., which was then coated with a thin varnish. When the varnish was nearly dry a stout sheet of tin-foil cut out to fit the area was laid on one side of the glass and pressed evenly down, the foil being left projecting at the upper edge to form a connexion.

A similar sheet of foil was fixed on one side of the other sheet of glass, and the two tin-foil electrodes were then held face to face in place by screw-clamps, the pressure on these being sufficient to reduce the space between the foil electrodes to 4·5 mm. For permanent use another insulator might be substituted for rubber which absorbs paraffin in time and swells.

Electrical Methods employed.

The current for the electrical measurements was provided by an oscillating valve arrangement G, which gave an alternating current at about 150 ~ and 1200 ~. Both frequencies were employed. A variable resistance of 100,000 ohms is shunted across the circuit, and this was adjusted until the voltage on

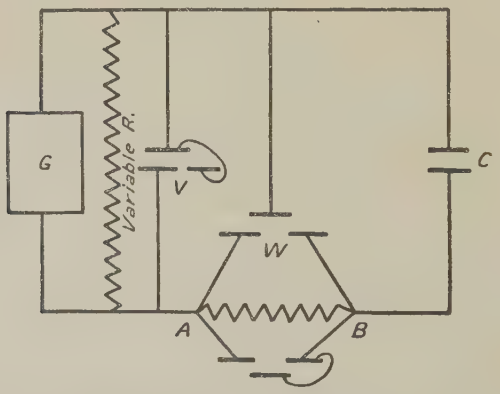
the condenser to be tested was maintained steadily at 110 volts, as shown by the electrostatic voltmeter V in the diagram.

G is the valve generating apparatus, DE the variable resistance of 100,000 ohms for regulating the circuit voltage.

V is the electrostatic voltmeter for preserving the P.D. across the circuit constant.

C is the condenser and AB a non-inductive resistance. Across this is a low reading electrostatic voltmeter which gave about 80 mm. deflexion for 1 volt between the terminals of AB, and the resistance of this being known therefore acts as an ammeter. AB was adjusted until a steady reading of about 200 mm. was obtainable on the ammeter.

Fig. 2.



The testing leads were now transferred from the condenser to a calibrated variable air-condenser, and the capacity of this was altered until the above reading was reproduced at the same voltage and frequency. The capacity indicated was then read off. It is free from capacity of the leads, is not influenced by any slight self-induction in AB, and though the valve should give nearly a sine wave, as the same wave form is used in both cases there should be no correction needed for this.

Measurements were first made on the empty condenser and then on the condenser filled, which gave the data for the calculations needed above.

Finally, before accepting the results, measurements under the same conditions were made with the electrostatic wattmeter.

The wattmeter W has a constant of about 40. That is,

with 110 volts on the needle, it gives a deflexion of about $\frac{110 \times 40}{10} = 440°$ for 1/10 volt drop between the quadrants at Unity power factor, or about 44° for a Power Factor of 1 per cent. at 1 volt drop across AB. I have already dealt with the working of this instrument on Low Power Factors (Electrician, Feb. 21, 1922).

This measurement, balancing out the capacity or reversible energy, gives separately the energy dissipated in leads, condenser itself, and the mixture; it also enables one to see that there is no abnormal leakage. The loss in this case was small, therefore the capacity measurement was practically free from the effects of absorption.

(As the result of long experience I find that absorption is always accompanied by dissipation of energy more or less directly proportionate to any increase of apparent capacity due to it. If, therefore, the loss is very small, being also at 90° phase difference with the capacity component of the current, we may conclude that the capacity found represents closely the true dielectric constant. See epitome of my lectures (Journal I. E. E. Jan. 1919, indexed under Institution Notes).

This method of mixture can also be applied to sheets of material. It obviates the necessity for guard rings, and from an educational point of view it brings into prominence the fact that the dielectric constant is primarily a Volume constant of matter.

LV. *On the Flow of Liquids into Capillary Tubes.* *By* C. H. Bosanquet, *M.A., Lee's Reader in Physics, Christ Church, Oxford* *.

THE equations of motion of a liquid flowing into a capillary tube under the influence of its surface tension and of a hydrostatic pressure have been examined in some detail by Washburn (Phys. Rev. xvii. p. 273, 1921). He obtains a formula giving the time taken by the meniscus to pass between two points in a straight uniform capillary inclined at any angle to the vertical.

In his treatment, forces due to changes of the momentum of the liquid column are neglected, and the object of the present paper is to examine the effects due to these forces, and determine under what circumstances they become inappreciable.

* Communicated by the Author.

The simplest case, which is capable of a rigorous solution if Poiseuille's law be assumed to hold, is that of a liquid flowing from a reservoir of large area into an evacuated horizontal capillary.

If P is the pressure at the entrance to the capillary, and the other symbols have the usual significance, then the accelerating force is $P\pi r^2 + 2\pi r T$, the viscous retarding force is $8\pi\eta x\dot{x}$ and the momentum of the liquid column $\pi r^2 \rho x\dot{x}$.

The equation of motion thus becomes :—

$$\frac{d}{dt}(\pi r^2 \rho x\dot{x}) + 8\pi\eta x\dot{x} = P\pi r^2 + 2\pi r T.$$

Let $$\frac{8\eta}{r^2\rho} = a, \qquad \frac{Pr + 2T}{r\rho} = b.$$

Then $$\frac{d}{dt} x\dot{x} + ax\dot{x} = b,$$

$$x\dot{x} = \frac{b}{a}(1 - e^{-at}) = \frac{1}{2} \cdot \frac{d}{dt} x^2.$$

$$\therefore \qquad x_2^2 - x_1^2 = \frac{2b}{a}\left\{ t - \frac{1}{a}(1 - e^{-at}) \right\}. \qquad . \quad . \quad . \quad (1)$$

This case was treated by Rideal in a recent paper (Phil. Mag. Dec. 1922, p. 1152) with rather different results. He writes his differential equation

$$x\ddot{x} + ax\dot{x} = b,$$

omitting a term in $(\dot{x})^2$ which represents the force required to impart momentum to the liquid entering the tube. As the result of this omission he obtains a different expression, which he gives as

$$t = \frac{a}{2b} x^2 - \frac{1}{a} \log x + \ldots .$$

From this he concludes that x is a linear function of $\sqrt{t}$ if x is neither very small nor very large, and his curves appear to be plotted on the assumption that

$$x_2 - x_1 = \sqrt{\frac{2bt}{a}} + \text{a constant}$$

as soon as a state of steady motion has been attained.

Owing to the fact that in his experiments x_1 was fairly small, he obtains a linear relation within the error of experiment for values of $x_2 > 2.x_1$, but the values of $\frac{T}{\eta}$ deduced

from the slope of the curves must be subject to a systematic error of six or seven per cent.

Equation (1) above reduces to that of Washburn if r is very small or if the meniscus is not timed from rest, but allowed to attain a state of steady motion before taking any readings.

In the case of ether in a capillary of 1 mm. diameter a has the value 10 $\sec^{-1}$ at about 20°, so that $\frac{1}{a}$ is negligible for tubes of smaller diameter. $a > 10$ for almost all other liquids in a 1 mm. capillary.

If the capillary has a total length l and initially contains a gas of viscosity η' and density ρ', the viscous resistance becomes $8\pi\dot{x}\{\eta x + \eta'(l-x)\}$, and the momentum of the contents of the tube $\pi r^2\dot{x}\{\rho x + \rho'(l-x)\}$.

Let $$\frac{l\eta'}{\eta-\eta'} = x_\eta, \qquad \frac{l\rho'}{\rho-\rho'} = x_\rho ;$$

then

$$\frac{d}{dt}(x+x_\rho)(\rho-\rho')\dot{x} + \frac{8}{r^2}(x+x_\eta)(\eta-\eta')\dot{x} = \mathrm{P} + \frac{2\mathrm{T}}{r},$$

if $(x+x_\eta) = \xi, \qquad (x_\eta - x_\rho) = \xi_0,$

then $$\frac{d}{dt}(\xi-\xi_0)\dot{\xi} + \alpha\xi\dot{\xi} = \beta. \quad . \quad . \quad . \quad . \quad (2)$$

As a first approximation $\dot{\xi} = \frac{\beta}{\alpha\xi}$ after the initial period of acceleration, so that

$$\frac{d}{dt}(\xi-\xi_0)\dot{\xi} = \frac{\beta^2\xi_0}{\alpha^2\xi^3},$$

Using this result,

$$\alpha\xi\dot{\xi} = \beta - \frac{\beta^2\xi_0}{\alpha^2\xi^3}.$$

Proceeding in this way by successive approximations a value of $\dot{\xi}$ is obtained which is less than $\frac{\beta}{\alpha\xi}$ if $x_\eta > x_\rho$,

$$t = \int \frac{d\xi}{\dot{\xi}},$$

$$\frac{1}{\dot{\xi}} = \frac{\alpha\xi}{\beta} + \frac{\xi_0}{\alpha\xi^2} + \frac{3\beta\xi_0}{\alpha^3\xi^4} - \frac{4\beta\xi_0^2}{\alpha^3\xi^5} + \frac{15\beta^2\xi_0}{\alpha^5\xi^6} - \frac{48\beta^2\xi_0^2}{\alpha^5\xi^7} + \frac{35\beta^2\xi_0^3}{\alpha^5\xi^8} + \ldots.$$

Then if the steady state has been attained by the time $\xi = \xi_1$

and ξ_2 is very large,

$$t = \frac{\alpha}{2\beta}(\xi_2^2-\xi_1^2)+\frac{1}{\alpha}\cdot\frac{\xi_0}{\xi_1}\left\{1+\frac{\beta}{\alpha^2\xi_1^2}\left(1-\frac{\xi_0}{\xi_1}\right)\right.$$
$$\left.+\frac{\beta^2}{\alpha^4\xi_1^4}\left(3-8\frac{\xi_0}{\xi_1}+5\frac{\xi_0^2}{\xi_1^2}\right)+\ldots.\right\},$$

or

$$t = \frac{\alpha}{2\beta}(\xi_2^2-\xi_1^2)+\frac{1}{\alpha}\phi(\xi_1). \quad . \quad . \quad . \quad . \quad (3)$$

If the density of the gas is negligible and the liquid starts from the end of the tube $\xi_1=\xi_0$ and $\phi(\xi_1)=1$,

$$t = \frac{\alpha}{2\beta}(\xi_2^2-\xi_0^2)+\frac{1}{\alpha}(1-\phi(\xi_2)). \quad . \quad . \quad . \quad (4)$$

In this case the steady state is attained instantaneously so that no time is lost in accelerating.

If ξ_1 is large compared with ξ_0, as a first approximation $\xi\dot{\xi}=\frac{\beta}{\alpha}(1-e^{-\alpha t})$,

$$\xi_0\ddot{\xi} = \frac{\xi_0}{\xi}\left(1+\frac{\beta}{\alpha^2\xi^2}\right)\frac{d}{dt}(\xi\dot{\xi})-\frac{\beta^2}{\alpha^2\xi^2}\cdot\frac{\xi_0}{\xi}.$$

Then from (2)

$$\frac{d}{dt}(\xi\dot{\xi}) = \beta-\alpha\xi\dot{\xi}+\xi_0\ddot{\xi},$$

$$\therefore \quad \frac{d}{dt}(\xi\dot{\xi}) = \frac{\beta\left(1-\frac{\beta}{\alpha^2\xi^2}\cdot\frac{\xi_0}{\xi}\right)-\alpha\xi\dot{\xi}}{1-\frac{\xi_0}{\xi}\left(1+\frac{\beta}{\alpha^2\xi^2}\right)}.$$

If $\frac{1}{\xi}$ does not change appreciably while the liquid is accelerating,

$$\xi\dot{\xi} = \left(\frac{\beta}{\alpha}-\frac{\beta^2}{\alpha^2\xi_1^2}\cdot\frac{\xi_0}{\xi_1}\right)\left(1-e^{-\frac{\alpha t}{1-\frac{\xi_0}{\xi_1}\left(1+\frac{\beta}{\alpha^2\xi_1^2}\right)}}\right)$$

to a first approximation,

and if ξ_2 is very large compared with ξ_0

$$t = \frac{\alpha}{2\beta}(\xi_2^2-\xi_1^2)+\frac{1}{\alpha}\cdot\frac{\xi_0}{\xi_1}\left(1+\frac{4\beta}{\alpha^2\xi_1^2}\cdot\frac{\xi_0}{\xi_1}+\ldots.\right)$$
$$+\frac{1}{\alpha}\left(1-\frac{\xi_0}{\xi_1}\left(1+\frac{\beta}{\alpha^2\xi_1^2}\right)\right)$$
$$=\frac{\alpha}{2\beta}(\xi_2^2-\xi_1^2)+\frac{1}{\alpha}\left(1-\frac{\xi_0}{\xi_1}\cdot\frac{\beta}{\alpha^2\xi_1^2}\left(1-\frac{4\xi_0}{\xi_1}\right)+\ldots.\right).$$

If ξ_1 is large the last term is very small, also it disappears on continuing the approximation, so that if the steady state is reached before $\xi=\xi_2$

$$t=\frac{\alpha}{2\beta}(\xi_2^2-\xi_1^2)+\frac{1}{\alpha}(1-\phi(\xi_2)).$$

This is identical with (4).

In general

$$t=\frac{\alpha}{2\beta}(\xi_2^2-\xi_1^2)+\frac{1}{\alpha}(1-\phi(\xi_2))-\frac{1}{\alpha}(1-\phi(\xi_1))e^{-\frac{\alpha t}{1-\phi(\xi_1)}+\cdots}$$

. . . . (5)

The subsequent terms in the exponential are terms in t^3 and higher powers of t.

Substituting for α, β, ξ,

$$t+\frac{r^2(\rho-\rho')}{8(\eta-\eta')}(1-\phi(x_1+x_\eta))\,e^{-8(\eta-\eta')t/r^2(\rho-\rho')(1-\phi(x_1+x_\eta))}$$

$$=\frac{4(\eta-\eta')}{2r\mathrm{T}+r^2\mathrm{P}}((x_2+x_\eta)^2-(x_1+x_\eta)^2)$$

$$+\frac{r^2(\rho-\rho')}{8(\eta-\eta')}(1-\phi(x_2+x_\eta)). \quad . \quad (6)$$

This reduces to (1) if η' and ρ' are put equal to zero, and to Washburn's equation if the second term on each side of the equation is omitted.

If the capillary is inclined upwards at an angle θ to the horizontal then, if $\gamma=g\sin\theta$, $\beta=\dfrac{\mathrm{P}r+\gamma rl\rho'+2\mathrm{T}}{r(\rho-\rho')}$, and $\mathrm{X}=\dfrac{\beta}{\gamma}+\xi_0-\xi$,

$$\frac{d}{dt}(\xi-\xi_0)\dot{\xi}+\alpha\xi\dot{\xi}=\beta-\gamma(\xi-\xi_0)=\gamma\mathrm{X}.$$

As a first approximation $\xi\dot{\xi}=\dfrac{\gamma}{\alpha}\mathrm{X}$,

$$\frac{d}{dt}(\xi-\xi_0)\dot{\xi}=\frac{\gamma}{\alpha}\left(1-\frac{\xi_0}{\xi}-\frac{\mathrm{X}\xi_0}{\xi^2}\right)\dot{\mathrm{X}},$$

$$\frac{1}{\dot{\xi}}=\frac{\alpha\xi}{\gamma\mathrm{X}}-\frac{1}{\alpha\mathrm{X}}+\frac{\xi_0}{\alpha\mathrm{X}\xi}+\frac{\xi_0}{\alpha\xi^2},$$

$$= \int_{X_2}^{X_1} \left(\frac{\alpha\beta}{\gamma^2 X} + \frac{\alpha\xi_0}{\gamma X} - \frac{\alpha}{\gamma} - \frac{1}{\alpha X} \right) dX$$

$$+ \frac{\xi_0}{\alpha} \int_{\xi_1}^{\xi_2} \left(\frac{1}{\frac{\beta}{\gamma}\xi + \xi_0\xi - \xi^2} + \frac{1}{\xi^2} \right) d\xi$$

$$= \left(\frac{\alpha\beta}{\gamma^2} + \frac{\alpha\xi_0}{\gamma} - \frac{1}{\alpha} \right) \log \frac{\beta + \gamma\xi_0 - \gamma\xi_1}{\beta + \gamma\xi_0 - \gamma\xi_2} - \frac{\alpha}{\gamma}(\xi_2 - \xi_1)$$

$$+ \frac{\xi_0}{\alpha} \left(\frac{1}{\xi_1} - \frac{1}{\xi_2} \right) + \frac{\gamma\xi_0}{\alpha(\beta + \gamma\xi_0)} \left(\log \frac{\beta + \gamma\xi_0 - \gamma\xi_1}{\beta + \gamma\xi_0 - \gamma\xi_2} - \log \frac{\xi_1 - \xi_0}{\xi_2 - \xi_0} \right)$$

. . . (7)

To this must be added a correction if the liquid starts from rest. The magnitude of the correction will be

$$\frac{1}{\alpha} \left(1 - \frac{\xi_0}{\xi_1} \right) \left(1 - e^{-\frac{\alpha\xi_1 t}{\xi_1 - \xi_0}} \right).$$

The time for a liquid starting from rest is thus given by :—

$$t + \frac{1}{\alpha} \left(1 - \frac{\xi_0}{\xi_1} \right) e^{-\frac{\alpha\xi_1 t}{\xi_1 - \xi_0}}$$

$$= \left(\frac{\alpha\beta}{\gamma^2} + \frac{\alpha\xi_0}{\gamma} - \frac{1}{\alpha} + \frac{\gamma\xi_0}{\alpha(\beta + \gamma\xi_0)} \right) \log \frac{\beta + \gamma\xi_0 - \gamma\xi_1}{\beta + \gamma\xi_0 - \gamma\xi_2}$$

$$- \frac{\alpha}{\gamma}(\xi_2 - \xi_1) + \frac{1}{\alpha} \left(1 - \frac{\xi_0}{\xi_2} \right) + \frac{\gamma\xi_0}{\alpha(\beta + \gamma\xi_0)} \log \frac{\xi_2 - \xi_0}{\xi_1 - \xi_0}. \quad (8)$$

This reduces to (5) if γ is vanishingly small and $\phi(\xi) = \frac{\xi_0}{\xi}$, and if the terms in $\frac{1}{\alpha}$ are omitted it reduces to Washburn's equation. Developing the series as far as first order terms in γ the formula becomes :—

$$t + \frac{1}{\alpha} \left(1 - \frac{\xi_0}{\xi_1} \right) e^{-\frac{\alpha\xi_1 t}{\xi_1 - \xi_0}}$$

$$= \frac{\alpha}{2\beta}(\xi_2^2 - \xi_1^2) + \frac{\alpha\gamma}{3\beta^2}(\xi_2^3 - \xi_1^3) - \frac{\gamma}{\alpha\beta}(\xi_2 - \xi_1) + \frac{1}{\alpha} \left(1 - \frac{\xi_0}{\xi_2} \right).$$

This form gives the effect due to a slight change of head with motion of the meniscus.

Observations of the rate of flow of a liquid into or out of a horizontal capillary under the influence of various initial values of P provide a method of determining both viscosity and surface tension. If t' is the value which the time would have if the density were zero, then

$$\frac{d\xi^2}{dt'} = \frac{r^2\mathrm{P} + 2r\mathrm{T}}{4\eta},$$

and measurements with two values of P yield both the viscosity and the surface tension.

The dynamic method of measuring surface tension has certain advantages over the static method ; the mean radius of the tube is required instead of the radius at one point, also the surface is being continuously renewed, thus reducing the risk of contamination. The method is also adaptable to the measurement of interfacial surface tensions and to the comparison of angles of contact with an advancing or receding meniscus.

In conclusion I wish to thank Professor F. A. Lindemann, F.R.S., for the interest which he has taken in this work.

Summary.

(1) The motion of a liquid flowing into a horizontal evacuated capillary under the influence of a constant head is examined and an expression is obtained which is rigorous if Poiseuille's law holds.

(2) The equations are extended to the case of two fluids in contact and an approximate solution is obtained.

(3) Similar formulæ are deduced for the case of a liquid flowing into an inclined tube.

LVI. *Temperature Measurement with the Einthoven Galvanometer.* *By* F. Adcock, *M.Sc., and* E. H. Wells, *M.Sc., late Bowen Research Scholars in Mechanical Engineering* *.

[Plates IX. & X.]

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The Object of the Present Work.

THE Einthoven galvanometer (see Pl. IX. fig. 1) has been used by a number of investigators † for the purpose of determining temperatures in the gas-engine cylinder, and their work clearly shows the practicability of recording quantitative results for the cycle of temperature in the heat-engine cylinder.

In order that the results recorded may be interpreted as temperature of the gas itself, it is necessary to know the relationship between the true temperature and the temperature assumed by the thermometer. It is the object of this research to investigate this relationship.

The difference between the temperature assumed by the thermometer and the temperature of the gas at any instant, which may be termed the "temperature lag," will depend

* Communicated by Prof. F. W. Burstall, M.Sc., M.A., M.Inst.C.E., M.I.Mech.E.

† For a history of Temperature Measurement in the Internal Combustion Engine, see the following:—

Burstall: "On the Measurement of Cyclically Varying Temperature," Phil. Mag., Sept. 1895.

B. Hopkinson: "On the Measurement of Gas Engine Temperatures," Phil. Mag., 1907.

Callendar and Dalby: "On the Measurement of Temperatures in the Cylinder of a Gas Engine," Proc. R. S., A lxx., 1908.

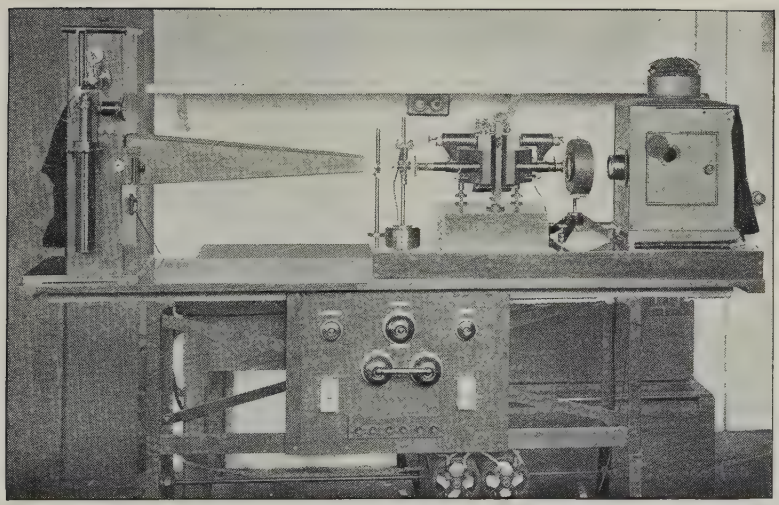
Coker and Scoble: Proc. Inst. C.E. vol. cxcvi., Part II., 1913-14.

Petersen: Verfahren zur Messung Schnell Wechselnder Temperaturen, 1913.

Nagel: Zeitschrift des Vereins Deutscher Ingenieure, 5th July, 1913.

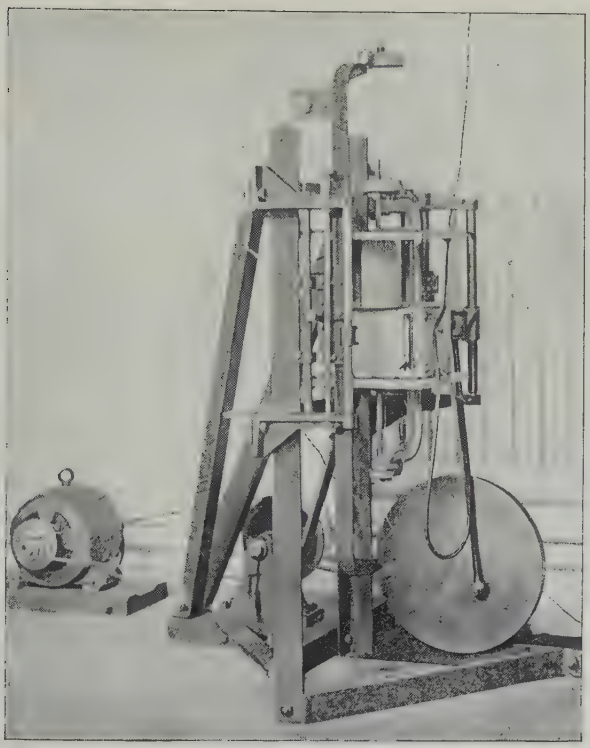
E. B. Wolff: Temperatuurmetingen in een Dieselmotor, 1913.

Fig. 1.



Photograph of Einthoven Galvanometer.

Fig. 3.



Photograph of Apparatus.

mainly on the following points, the effects of which require investigation :—

(1) The form of the thermometer employed.
(2) The rate of variation of temperature of the gas.
(3) The nature and temperature of the walls of the containing vessel.
(4) The velocity of gas relative to the thermometer.

It is intended that the thermometer which will be employed in the gas engine shall be of the type used in Professor Burstall's earlier work, *i. e.* the platinum resistance thermometer. The investigation, therefore, refers primarily to the platinum resistance thermometer, and apparatus has been designed and constructed accordingly.

The scheme adopted consists of maintaining steady temperatures of different intensity in different regions and moving the thermometer through these regions to obtain the cyclical variation of temperature ; the rate of variation of temperature is determined by the frequency of movement of the thermometer through the different temperature regions, and this can be varied within wide limits.

To study the effect of point (3), different methods of heating and cooling in the respective regions must be employed. The first type of apparatus embodies a vertical silica tube of which the upper part is wound with an electrical resistance heater, and the lower part is enclosed in a box through which water can be circulated. The thermometer can be reciprocated axially in the interior of the silica tube. Precautions are taken to reduce motion of the air in the tube to the minimum, and the natural convection tends to the same end ; but it is clear that the heating of the thermometer is largely by radiation from the walls of the silica tube.

Further work will be necessary to determine the effect of conditions such as those obtaining in the gas-engine cylinder, viz. cold walls and hot gas. These conditions would be approximated in an apparatus wherein a current of heated air and a current of air at atmospheric temperature pass along adjacent channels, the walls of which are water-jacketed. The thermometer would reciprocate between the two channels.

The effect of varying the velocity of gas relative to the thermometer may be studied in the apparatus under consideration by varying the frequency of reciprocation of the thermometer, and, to avoid changing the rate of variation of

the temperature at the same time, the limits of temperature may be varied as necessary.

In the design of the experimental thermometer it was necessary to provide for the fulfillment of the following conditions as closely as possible.

The carrying device must be light in weight so that the inertia when moving the thermometer at considerable speeds should not be excessive.

The air through which the thermometer moves should be disturbed as little as possible by the reciprocation of the thermometer.

Conditions favouring the formation of a pocket of air round the thermometer and carried with it must be avoided.

The temperature throughout the path of the thermometer travel must be known, and means must be provided for independent measurement of this while the thermometer is reciprocating.

The whole of the thermometer must be in a region of uniform temperature at any instant, and the compensating leads must be at the same temperature as the main leads at any corresponding part of their length.

Description of the Apparatus.

A silica tube (1) (see fig. 2 and Pl. X. fig. 3), of two inches internal diameter and twelve inches long, is mounted vertically between two hard asbestos sheets (2), which are bolted to brackets on the main framework. The upper part of the silica tube is wound with a resistance coil (3) embedded in Alundum cement, and lagged with non-conducting material (4).

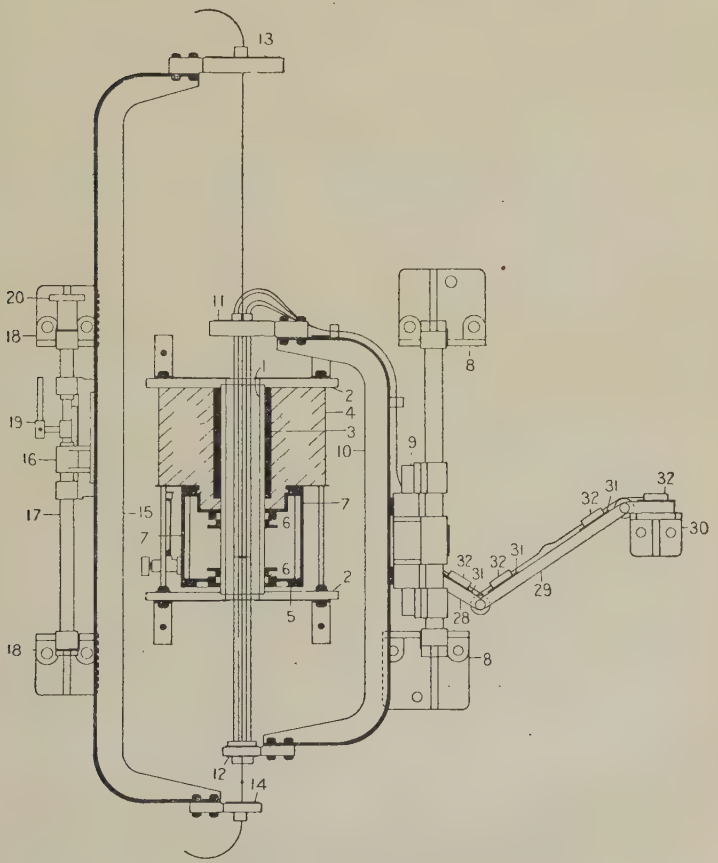
The lower part of the silica tube is enclosed by a water vessel (5) which has glands (6) packed with asbestos. Access to the glands is obtained by removing the sides of the water vessel (7). Provision is made so that water may be circulated through the vessel, the overflow being near the top.

The brackets (8) carry slide-bars on which the cross-head (9) reciprocates. A pointer and scale are provided to indicate the position of the cross-head with respect to the main frame and the stroke length. The frame (10) is bolted to the cross-head and carries the insulating heads (11) and (12). Between pairs of terminals on the insulating heads (11) and (12) run four carrying wires through the interior of the silica tube. The thermometer wire spans two of the carrying

wires and two more are bridged to form a compensating circuit.

The carrying wires are placed in such positions that the fine thermometer wire is about one inch long and the fine wire in the compensator circuit about half an inch long.

Fig. 2.



Sectional Elevation of Apparatus.

Short pieces, about 0·1 in. long, of platinum wire, 0·01 in. diameter, are silver soldered to the carrying wires and the fine platinum wire in each circuit is gold soldered to these short pieces. The two circuits are made exactly similar except for the difference in length of the fine platinum wire. This difference is the length of platinum wire in the ideal

resistance thermometer to which the experimental thermometer corresponds. The platinum wires in the two circuits lie in one plane normal to the axis of the silica tube so that they shall be as nearly as possible at the same temperature.

Between the fine wires in the thermometer and compensator circuits, a fine wire thermocouple is carried inside the silica tube by the insulating heads (13) and (14) attached to the frame (15). This is capable of independent movement parallel to the motion of the thermometer by movement of the slider (16) on the slide-bars (17), which are carried by brackets (18) on the main framework. This slider can be clamped at any part of its travel by a clamping bolt (19), and small movements can be effected by rotating the knob (20). A pointer attached to the slider registers positions of the thermocouple by means of a scale fixed to the main framework.

The procedure in mounting the thermometer and thermocouple is as follows :—A steel rod is passed through a hole provided in the head (11) and into the silica tube and then screwed into the head (12), after which the head (11) is secured to the rod. The steel rod thus forms an auxiliary frame by means of which, after releasing the fixing screws, the insulating heads are removed from the frame (10). The upper thermocouple head (13) is removed from the frame (15) to allow the auxiliary frame to be lifted vertically clear of the apparatus.

The carrying wires for the thermometer are mounted between the insulating heads (11) and (12) and the fine wires are soldered to them. The thermocouple is mounted up, being temporarily attached to the heads (11) and (12). The thermojunction and the fine wires of the thermometer and compensator circuits are arranged to be all in the same plane. When this assembly is complete it is inserted through the silica tube and the insulating heads are attached to the frame (10), after which the steel rod is detached and removed. The cross-head is brought to the middle of its stroke and the thermocouple slider to its mid-position, and the readings on the respective scales are noted. The thermocouple is attached to the insulating heads (13) and (14) and then released from the thermometer assembly. The thermocouple can be brought to any desired point in the stroke of the thermometer by reference to the two initial readings.

The thermometer may at any time be removed from the apparatus for inspection by inserting the steel rod and fixing to it the heads (11) and (12) and releasing them from the frame (10); but the thermocouple must first be clamped to these heads and released from its insulating heads (13) and (14).

The cross-head (9) of the thermometer frame is actuated through a connecting-rod by a crank pin on the crank disk (see Pl. X. fig. 3). The crank disk functions as a flywheel, giving a small coefficient of irregularity of angular velocity at high speed. Balance weights are formed integral with the crank disk so that a static balance of the reciprocating parts is obtained, giving a small coefficient of irregularity of angular velocity at slow speeds.

The crank disk is carried on a shaft running in the two bearings of a pedestal and the shaft is driven by a pulley. A similar pedestal is mounted on the framework and carries a countershaft. A flat leather belt runs on a pulley on the countershaft and the pulley on the main shaft, giving a speed reduction of four to one. An electric motor which runs at maximum speed of 1350 r.p.m. drives the apparatus by a cotton driving-rope running over a pair of grooved pulleys having five steps, giving a series of speeds which form an arithmetic progression. One cone pulley is keyed to the countershaft and the other is carried on the motor shaft. After a number of experiments had been carried out, another shaft with a pair of pulleys was introduced between the countershaft shown in Pl. X. fig. 3 and the main shaft in order to give further reduction in speed.

Speed regulation of the motor is obtained by means of a rheostat in the armature circuit which can be connected either as a potentiometer or as a series resistance.

Four leads from the insulating head (11) to some fixed part of the apparatus are required to connect the thermometer and compensating circuits to the bridge. It is of great importance that the resistance of these leads should be unaffected by the reciprocation, so that sliding contacts cannot be used. Two swinging links (28) and (29) connect the cross-head to a bracket (30) on the main framework. Insulating blocks (31) are screwed to the cross-head, the two swinging links, and the bracket; and groups of four terminals (32) are attached to each insulating block.

Coiled around the axis pin of each moving joint, a helix of springy brass wire connects each corresponding pair of terminals. Movement of the cross-head produces flexion in the wire of the helix, but the strain is kept low and no change in resistance can be detected. From the terminals on the fixed bracket (30) stout leads are taken to the Wheatstone's bridge.

In order to register the temperature readings on the photographic plate with respect to the position of the thermometer in its stroke, a small pointer was attached to the

armature of an electromagnet which was mounted on the front of the camera. The electric circuit through this magnet was completed by a contact made at the top and bottom of the stroke, thus producing a continuous line on the plate with a small kick each time the current was allowed to pass. For this idea the authors are indebted to Dr. E. B. Wolff (Temperatuurmetingen in een Dieselmotor, 1913).

The Mathematical Theory of the Unbalanced Wheatstone's Bridge.

In fig. 4, let P, Q, R, and S be the resistance of the four arms of the bridge, and G the resistance of the galvanometer. Let e be the potential difference across the bridge

Fig. 4.

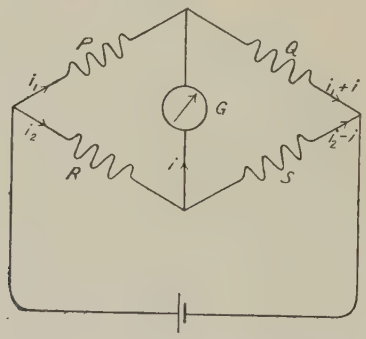


Diagram of Wheatstone's Bridge.

and v the potential difference across the galvanometer. Let i_1 be the current in P, i_2 the current in R, and i the current in the galvanometer.

The current in Q will be i_1+i.
The current in S will be i_2-i.
The potential difference across P will be i_1P.
The potential difference across Q will be (i_1+i)Q.
The potential difference across R will be i_2R.
The potential difference across S will be (i_2-i)S.
The potential difference across G will be iG.

The three currents i_1, i_2, and i are connected by the following three equations :—

Sum of p.d.'s across P and Q, $i_1\mathrm{P}+(i_1+i)\mathrm{Q}=e$. . (1)

Sum of p.d.'s across R and S, $i_2\mathrm{R}+(i_2-i)\mathrm{S}=e$. . (2)

Dif. of p.d.'s across P and R, $i_1\mathrm{P}-i_2\mathrm{R}=v=i\mathrm{G}$. (3)

These three equations are now to be solved.

From (1) and (3),

$$i_1\mathrm{P}+\left(i_1+\frac{i_1\mathrm{P}-i_2\mathrm{R}}{\mathrm{G}}\right)\mathrm{Q}=e. \quad . \quad . \quad . \quad . \quad . \quad (4)$$

From (2) and (3),

$$i_2\mathrm{R}+\left(i_2-\frac{i_1\mathrm{P}-i_2\mathrm{R}}{\mathrm{G}}\right)\mathrm{S}=e. \quad . \quad . \quad . \quad . \quad (5)$$

From (4),

$$i_1\mathrm{PG}+i_1\mathrm{GQ}-i_2\mathrm{RQ}+i_1\mathrm{PQ}=e\mathrm{G},$$

$$i_1(\mathrm{PG}+\mathrm{GQ}+\mathrm{PQ})-i_2\mathrm{RQ}=e\mathrm{G}. \quad . \quad . \quad . \quad (6)$$

From (5),

$$i_2\mathrm{RG}+i_2\mathrm{GS}+i_2\mathrm{RS}-i_1\mathrm{PS}=e\mathrm{G},$$

$$i_2(\mathrm{RG}+\mathrm{GS}+\mathrm{RS})-i_1\mathrm{PS}=e\mathrm{G}. \quad . \quad . \quad . \quad (7)$$

From (6),

$$i_1(\mathrm{P^2SG}+\mathrm{PQSG}+\mathrm{P^2QS})-i_2\mathrm{PQRS}=e\mathrm{PSG}. \quad . \quad (8)$$

From (7),

$$-i_1(\mathrm{P^2SG}+\mathrm{PQSG}+\mathrm{P^2QS})+i_2(\mathrm{PRG^2}+\mathrm{QRG^2}+\mathrm{PQRG}+\mathrm{PSG^2}+\mathrm{QSG^2}+\mathrm{PQSG}+\mathrm{PRSG}+\mathrm{QRSG}+\mathrm{PQRS})=e\mathrm{G^2P}+e\mathrm{G^2Q}+e\mathrm{GPQ}. \quad . \quad . \quad . \quad (9)$$

From (8) and (9),

$$i_2(\mathrm{PRG^2}+\mathrm{QRG^2}+\mathrm{PQRG}+\mathrm{PSG^2}+\mathrm{QSG^2}+\mathrm{PQSG}+\mathrm{PRSG}+\mathrm{QRSG})=e\mathrm{PSG}+e\mathrm{G^2P}+e\mathrm{G^2Q}+e\mathrm{GPQ},$$

$$i_2=e\frac{\mathrm{PS}+\mathrm{GP}+\mathrm{GQ}+\mathrm{PQ}}{\mathrm{PRG}+\mathrm{QRG}+\mathrm{PQR}+\mathrm{PSG}+\mathrm{QSG}+\mathrm{PQS}+\mathrm{PRS}+\mathrm{QRS}}. \quad (10)$$

From (7) and (10),

$$i_1\mathrm{PS}=e\left(\frac{(\mathrm{RG}+\mathrm{GS}+\mathrm{RS})(\mathrm{PS}+\mathrm{GP}+\mathrm{GQ}+\mathrm{PQ})}{\mathrm{PRG}+\mathrm{QRG}+\mathrm{PQR}+\mathrm{PSG}+\mathrm{QSG}+\mathrm{PQS}+\mathrm{PRS}+\mathrm{QRS}}-\mathrm{G}\right)$$

$$=e\left(\frac{+\mathrm{QSG^2}+\mathrm{PQSG}+\mathrm{PRS^2}+\mathrm{QRSG}+\mathrm{PQRS}}{\mathrm{PRG}+\mathrm{QRG}+\mathrm{PQR}+\mathrm{PSG}+\mathrm{QSG}+\mathrm{PQS}+\mathrm{PRS}+\mathrm{QRS}}\right.$$

$$\left.\frac{2\mathrm{PRSG}+\mathrm{PRG^2}+\mathrm{QRG^2}+\mathrm{PQRG}+\mathrm{PGS^2}+\mathrm{PSG^2}}{\mathrm{PRG}+\mathrm{QRG}+\mathrm{PQR}+\mathrm{PSG}+\mathrm{QSG}+\mathrm{PQS}+\mathrm{PRS}+\mathrm{QRS}}-\mathrm{G}\right)$$

$$=e\frac{\mathrm{PQRS}+\mathrm{PRSG}+\mathrm{PGS^2}+\mathrm{PRS^2}}{\mathrm{PRG}+\mathrm{QRG}+\mathrm{PQR}+\mathrm{PSG}+\mathrm{QSG}+\mathrm{PQS}+\mathrm{PRS}+\mathrm{QRS}}$$

$$i_1=e\frac{\mathrm{QR}+\mathrm{RG}+\mathrm{GS}+\mathrm{RS}}{\mathrm{PRG}+\mathrm{QRG}+\mathrm{PQR}+\mathrm{PSG}+\mathrm{QSG}+\mathrm{PQS}+\mathrm{PRS}+\mathrm{QRS}}. \quad (11)$$

From (10), (11), and (3),

$$v = iG = e\frac{\begin{matrix}-QRG-PQR\\ PQR+RPG+PSG+PRS-PRS-PRG\end{matrix}}{\begin{matrix}PRG+QRG+PQR+PSG+QSG+PQS\\ +PRS+QRS\end{matrix}}$$

$$= e\frac{PSG-QRG}{\begin{matrix}PRG+QRG+PQR+PSG+QSG+PQS\\ +PRS+QRS\end{matrix}} \quad (12)$$

$$i = e\frac{PS-QR}{\begin{matrix}RPG+QRG+PQR+PSG+QSG+PQS\\ +PRS+QRS\end{matrix}} \quad (13)$$

Application to Resistance Thermometer.

In the ordinary form of resistance thermometer, a resistance wire is inserted in the arm P of the bridge, and a pair of compensating leads is inserted in the arm Q to neutralize the effect of change in resistance of the main leads. In order that the compensation shall be accurate it is necessary that the resistance S bear to R the same ratio as the resistance of the compensating leads bears to the resistance of the main leads, and the balance obtained by adding extra resistance to the Q arm. It is convenient to make the compensating leads exactly similar to the main leads and this necessitates R and S being equal. When a balance is obtained, therefore, $P=Q$. When a balance is not obtained, the p.d. across the galvanometer is given, from equation (12), by

$$v = e\frac{(P-Q)G}{(P+Q)(2G+R)+2PQ}$$

$$= e\frac{P-Q}{\left(2+\frac{R}{G}\right)(P+Q)+\frac{2}{G}PQ} \quad . \quad . \quad (14)$$

This method of connecting up the Wheatstone's bridge may be termed a "series" arrangement, since the thermometer and compensating circuits are in series with respect to the battery current. If we interchange the battery and galvanometer we obtain what may be termed a "parallel" arrangement, since the thermometer and compensating circuits will now be in parallel with respect to the battery

current. This method of connecting up will now be considered. The most convenient way to do this is to interchange P and S in equation (12). This gives

$$v = e\frac{SPG-QRG}{SRG+QRG+SQR+SPG+QPG+SQP+SRP+QRP}.$$

Putting $S=R$,

$$v = e\frac{RPG-QRG}{R^2G+QRG+R^2Q+RPG+QPG+RQP+R^2P+QRP}$$

$$= e\frac{(P-Q)RG}{R^2(P+Q+G)+RG(P+Q)+PQ(2R+G)}$$

$$= e\frac{(P-Q)RG}{(P+Q)(R^2+RG)+R^2G+PQ(2R+G)}$$

$$= e\frac{P-Q}{\left(1+\frac{R}{G}\right)(P+Q)+R+\left(\frac{2}{G}+\frac{1}{R}\right)PQ} \quad . \quad . \quad (15)$$

The Relative Advantages of "Series" and "Parallel" Arrangements.

In the resistance thermometer as generally used, for example, in the Callendar Temperature Recorder, a slide wire is inserted between P and Q, and a connexion is made by means of a jockey at a balance point. Under these circumstances it is considered preferable that the sliding contact should not carry the main current, so the "series" arrangement is adopted, whereby the jockey only carries the galvanometer current, which is of necessity always small, and which vanishes when a balance is obtained.

For measuring cyclically varying temperatures, however, the slide wire is not necessary and other matters exert their claim for consideration, namely, the battery heating of the thermometer wire and the efficacy of the compensating circuit.

Prof. G. Forbes gives for bare overhead wires :—

$$\text{Current} = \sqrt{\frac{d^3 t}{320\,\mathrm{R}}},$$

where d = diameter of wire in cms.

t = difference in temperature between wire and air in ° C.

and R = specific resistance of wire at limiting temperature in ohms per cm. cube.

According to this formula, if the specific resistance of platinum be assumed to be 44×10^{-6} ohm per cm. cube at 1000° C., and the temperature difference be limited to 5° C., the current in the thermometer wire will be as follows :—

Dia. of thermometer wire. inches.	Current. amperes.
·01	·0764
·00585	·0342
·0032	·0138
·0025	·00958
·002	·00685
·0015	·00445
·001	·00242

In all the theoretical calculations, this is assumed to be the maximum safe current, and this forms the basis of the comparison between the different arrangements and between different values of the resistances R and G in equations (14) and (15).

If this current be constant, as it will be very nearly if the platinum resistance forms only a small part of the resistance of the whole circuit, the temperature difference when the platinum is at 0° C. (taking the specific resistance as 11×10^{-6} ohm per cm. cube) is found by the same formula to be 1·25° C.

Thus, if this value be adopted, the heating of the platinum due to battery current is quite negligible.

Compensation.

It will be noticed that in both equations (14) and (15) the expressions (P + Q) and PQ occur in the denominator,

consequently any increase in resistance which affects P and Q equally reduces the p.d. across the galvanometer—in other words, the compensators do not compensate except when a balance is obtained. This is a serious matter when using the Wheatstone's bridge for measuring cyclically varying temperatures, and its effect will now be considered.

It can be proved that when R is greater than P the parallel arrangement gives greater sensitivity and better compensation than the series, and that when R is less than P the series arrangement gives greater sensitivity and better compensation than the parallel.

This is best illustrated by taking an actual case. The expressions for v in equations (14) and (15) involve five quantities, e, R, G, P, and Q. Of these, P and Q, only, vary with the temperature of the thermometer; the remainder can have any values assigned to them, but, when once decided upon, remain constant throughout the experiment.

The method adopted for treating the problem mathematically is to obtain a balance when the thermometer is at 0° C. and calculate the p.d. across the galvanometer produced when the thermometer is at 1000° C. This is done for various values of e, R, and G, and for the series and parallel arrangements.

These results are plotted in figs. 5 and 6 for an experimental thermometer the particulars of which are as follows:—

Dia. of thermometer wire ·0032 inch.

P circuit includes platinum the resistance of which at 0° C. is ·51 ohm.

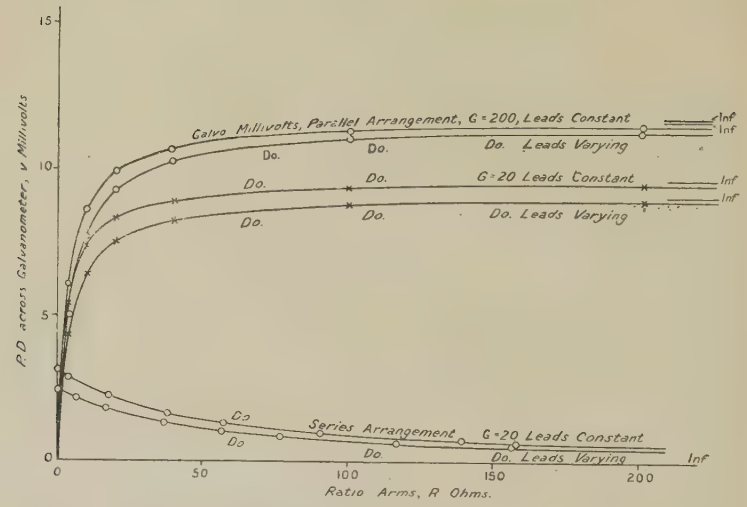
Q circuit includes platinum the resistance of which at 0° C. is ·22 ohm.

Q circuit includes external resistance of ·29 ohm in order to obtain a balance at 0° C.

Each circuit includes leads the resistance of which at 0° C. is ·88 ohm.

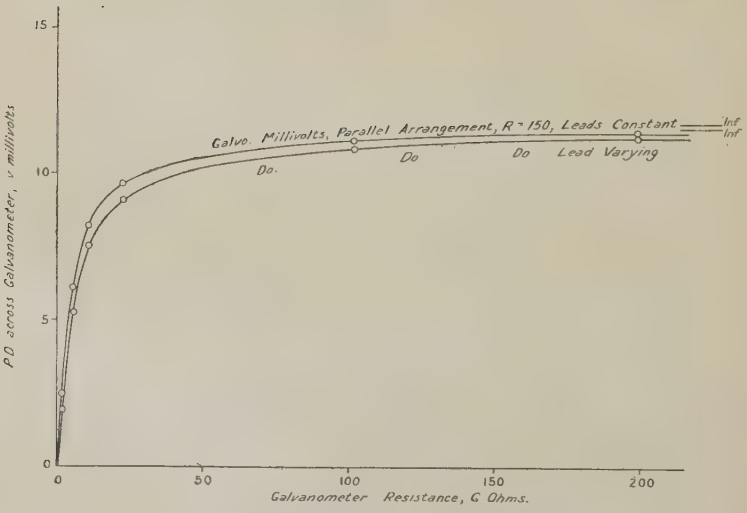
In order to find the effect of a change in resistance in leads, the resistance of the leads is assumed to increase by ·66 ohm for the curves marked "leads varying." This increase in resistance would be occasioned by a length of 3 inches of the steel carrying wires, with which the experimental thermometer was originally mounted up, assuming the same temperature as the platinum.

Fig. 5.



Curve showing v against R.

Fig. 6.


P.D across Galvanometer, v millivolts
Galvo. Millivolts, Parallel Arrangement, R=150, Leads Constant
Do Lead Varying
Inf
Galvanometer Resistance, G Ohms.

Curve showing v against G.

Tables showing Error due to Heating of Carrying Wires.

Series Arrangement, G = 20 ohms.

R ohms.	Error per cent.
0	22·4
10	22·1
20	21·9
30	21·8
40	21·7
50	21·6
60	21·5
80	21·4
100	21·3
150	21·2
200	21·1
inf.	20·9

Parallel Arrangement, G = 20 ohms.

R ohms.	Error per cent.
0	—
1	27·2
4	19·9
10	13·5
20	9·4
40	7·3
100	6·0
200	5·5
inf.	4·9

Tables showing Error due to Heating of Carrying Wires.

Parallel Arrangement, G = 200 ohms.

R ohms.	Error per cent.
0	—
1	29·8
4	18·1
10	10·5
20	6·4
40	3·7
100	2·2
200	1·7
inf.	·85

Parallel Arrangement. R = 150 ohms.

G ohms.	Error per cent.
0	—
1	18·5
5	13·0
10	8·7
20	5·7
100	2·2
200	1·5
1000	1·04
4000	·97
inf.	·93

From calculations and these curves (figs. 5 and 6), the following deductions have been drawn :—

1. If R is greater than P, the parallel arrangement requires a higher e.m.f. than the series.
2. If R is greater than P, the parallel arrangement gives a greater sensitivity than the series.

3. If R is greater than P, the parallel arrangement gives better compensation than the series.
4. With the series arrangement, greater sensitivity is obtained with a small value for R.
5. With the parallel arrangement, greater sensitivity is obtained with a large value for R, but very little is gained by increasing R beyond 150 ohms.
6. With the series arrangement, better compensation is obtained with a large value for R, but the improvement is small.
7. With the parallel arrangement, better compensation is obtained with a large value for R, but very little is gained by increasing R beyond 150 ohms.
8. For fibres which give the same deflexion per millivolt, greater sensitivity and better compensation are obtained with a high resistance fibre, but in neither case is there much to be gained by increasing G beyond 200 ohms.

The fibres supplied for use in the galvanometer had a resistance of the order of 20 ohms; the curves have, therefore, been drawn for this value and also for 200 ohms.

In view of these deductions, it was decided to adopt the parallel arrangement, and make R equal to 150 ohms. This value has the advantage of requiring an e.m.f. which is very conveniently obtained, namely, 2·09 volts, or the e.m.f. of one accumulator cell.

For other diameters of thermometer wire and a 20-ohm fibre the corresponding values are as follows:—

Diameter. ins.	R ohms.	e volts.	v for 1000° C. volts.
·01	50	4	·0058
·00585	150	4	·0060
·0032	150	2	·0094
·0025	200	2	·0097
·002	300	2	·0098
·0015	400	2	·0094
·001	800	2	·0076

In view of the fact that the compensation is not exact when the bridge is unbalanced, it is important that the carrying wires should change their resistance by as small an amount as possible. After some trials copper was selected

as the most suitable material for two reasons: first, because its specific resistance is so low that any change in resistance is small compared with the platinum resistance, and, secondly, because its thermo e.m.f. with platinum is very small. The error due to heating of copper carrying wires is ·85 per cent. against 5·7 per cent. for the stainless steel under the conditions adopted for the experiments.

The extent of the variation in the resistance of the leads and carrying wires can be halved by adopting the Siemens three-lead arrangement. As the variation in the resistance of the common lead will in general be negligible compared with the ratio-arms, the error due to heating of the carrying wires will consequently also be about halved.

The reason why the three-lead arrangement was not adopted in the present experiments was because it was thought desirable to make the thermocouple and resistance thermometer as symmetrical as possible, and a three-lead resistance thermometer would have been difficult to arrange symmetrically with respect to the thermocouple.

This objection would not hold in the case of a thermometer intended for use in a gas engine or in a gas engine type of apparatus, and it is therefore suggested that if experiments are carried out in a gas engine or gas engine type of apparatus the three-lead arrangement should be adopted.

Experimental Results.

The procedure in making a set of tests was as follows. The resistance thermometer was set at the bottom of its stroke, that is in the cold part of the furnace tube, and the external resistance in the Q circuit was adjusted till an approximate balance was obtained, using the millivoltmeter in the bridge to avoid damaging the Einthoven fibre.

The Einthoven galvanometer was then connected to the bridge in place of the millivoltmeter and the latter was connected to the thermocouple.

By means of the scales provided for the purpose, the silica tube was explored with the resistance thermometer and thermocouple side by side. This provided both the stationary temperature distribution and the calibration of the resistance thermometer.

The resistance thermometer was then reciprocated by the motor and the speed counted by means of a stop-watch,

A loaded dark slide was inserted in the camera and the dashpot controlling the speed of fall of the plate carrier was adjusted so that between one and two cycles appeared on the plate.

After opening the dark slide the battery key was depressed and the plate allowed to fall, recording the galvanometer deflexion.

By means of a special stop having three steps the plate was brought to rest a short distance before the end of the plate had passed the slit. The battery key was released and the plate allowed to fall until the second step of the stop came into action, giving the zero position of the fibre. The motor was then shut down and the resistance thermometer set at the bottom of its stroke. With the battery key depressed the plate was allowed to fall until the third step of the stop came into action, giving the lower limit of temperature. The resistance thermometer was then moved to the top of its stroke, the battery key depressed, and the plate allowed to complete its fall, giving the upper limit of temperature. The battery key was released, the dark slide closed and taken out of the camera for development.

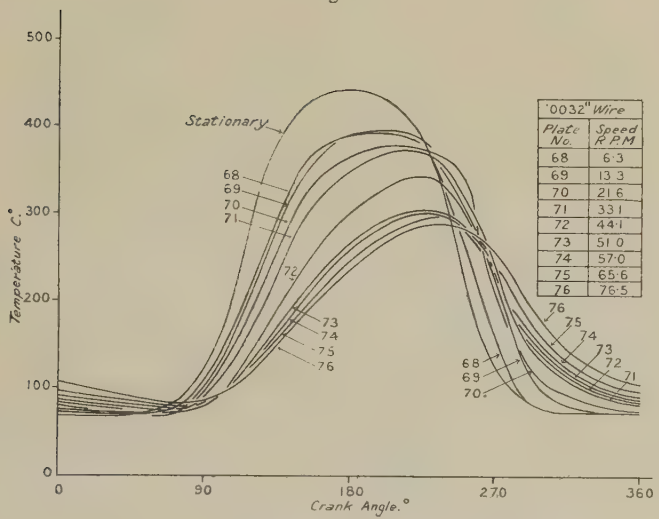
Thus each record consists of a wave and three discontinuous straight lines. The object of the zero position is obvious. The temperature limits are required to check variations in the voltage of the mains, and to correct the sensitivity accordingly.

Prints were taken from the plates and the interval between successive dead centres as indicated by the pointer in front of the camera was divided into intervals of 20 degrees of angle. The ordinates corresponding to these abscissæ were read and by reference to the calibration curve translated into temperatures.

Then all the curves corresponding to one set of tests, including the stationary temperature distribution, were plotted on the same crank angle base.

Figs. 7–15 show these resultant diagrams. The greatest discrepancy between the curve taken at speed and the stationary temperature distribution curve occurs at the upper dead centre. This is termed the temperature lag and is taken as a measure of the ability of the thermometer to follow the temperature changes.

Fig. 7.



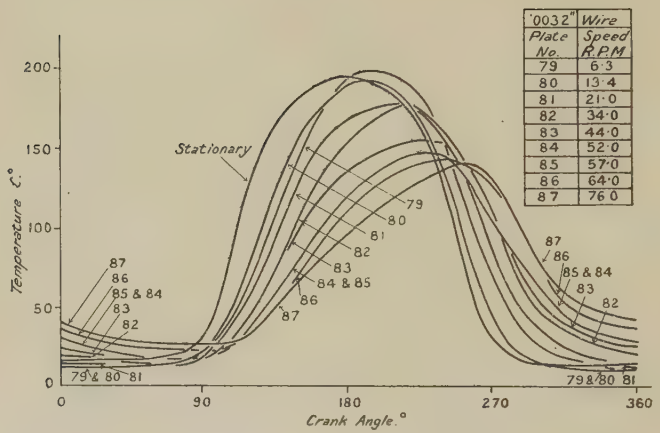
Experimental Curves, ·0032 in. measuring wire.

·0032 in. Wire.

Temperature Range 370° C.

Plate. No.	Lag. ° C.	$\frac{\text{Lag}}{\text{Range}}$.	Speed. r.p.m.
68	55·1	·15	6·3
69	51	·14	13·3
70	78·5	·21	21·6
71	92	·25	33·1
72	139	·38	44·1
73	176	·48	51·0
74	185	·50	57·0
75	197	·53	65·6
76	205	·56	76·5

Fig. 9.



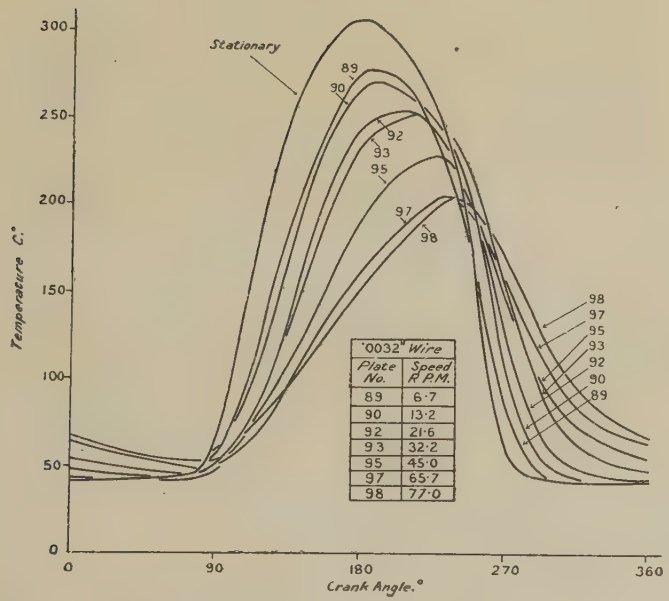
Experimental Curves, ·0032 in. measuring wire.

·0032 in. Wire.

Temperature Range 180° C.

Plate. No.	Lag. ° C.	Lag / Range	Speed. r.p.m.
79	2·5	·01	6·3
80	6	·03	13·4
81	30	·17	21
82	40	·22	34
83	60	·33	44
84	77·5	·43	52
85	77·5	·43	57
86	85	·47	64
87	100	·56	76

Fig. 9.



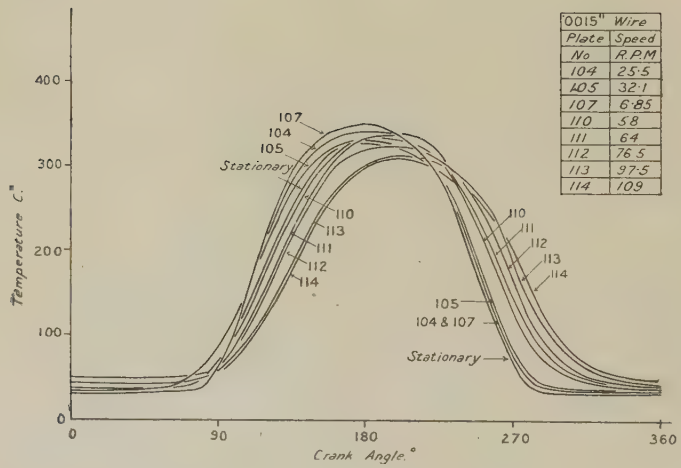
Experimental Curves, ·0032 in. measuring wire.

·0032 in. Wire.

Temperature Range 260° C.

Plate. No.	Lag. ° C.	$\frac{\text{Lag}}{\text{Range}}$	Speed. r.p.m.
89	31	·12	6·7
90	40	·15	13·2
92	60	·23	21·6
93	75	·29	32·2
95	110	·42	45·0
97	143	·55	65·7
98	154	·59	77·0

Fig. 10.



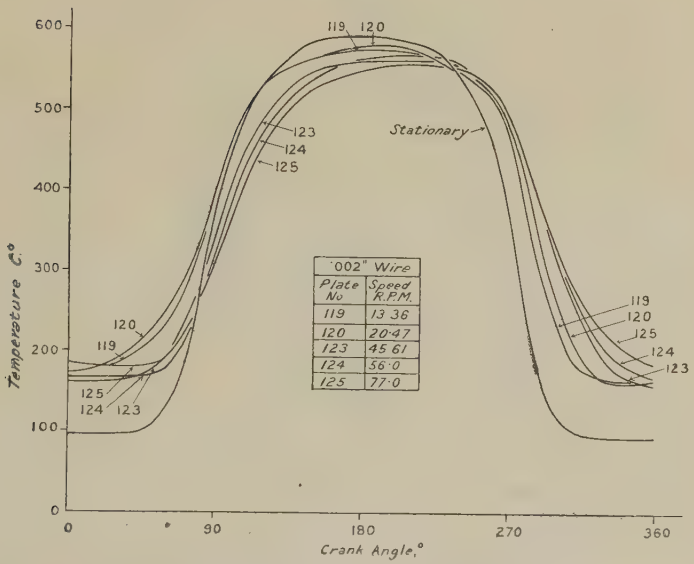
Experimental Curves, ·0015 in. measuring wire.

·0015 in. Wire.

Temperature Range 314° C.

Plate. No.	Lag. ° C.	$\frac{\text{Lag}}{\text{Range}}$.	Speed. r.p.m.
104	9·5	·03	25·5
105	19	·06	32·2
107	19	·06	6·9
110	19	·06	58·0
111	19	·06	64·0
112	41	·13	76·5
113	50·5	·16	97·5
114	55	·18	109·0

Fig. 11.



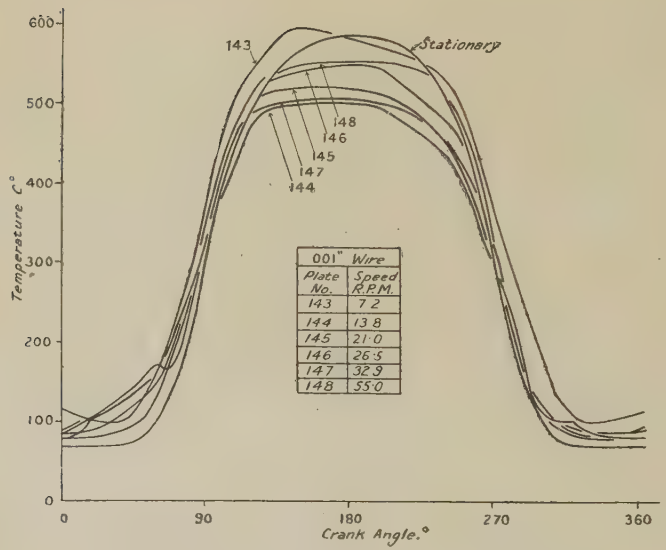
Experimental Curves, ·002 in. measuring wire.

·002 in. Wire.

Temperature Range 495° C.

Plate. No.	Lag. ° C.	$\frac{\text{Lag}}{\text{Range}}$.	Speed. r.p.m.
119	15	·03	13·4
120	10	·02	20·5
123	32	·06	45·6
124	28	·06	56
125	40	·08	77

Fig. 12.



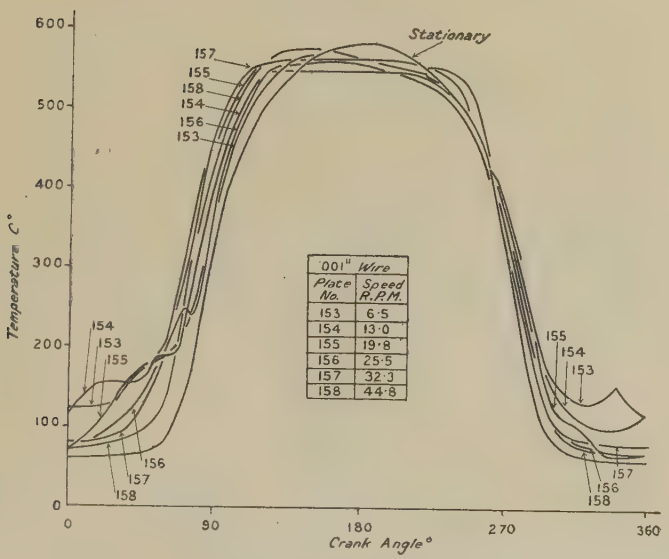
Experimental Curves, ·001 in. measuring wire.

·001 in. Wire.

Temperature Range 510° C.

Plate. No.	Lag. ° C.	$\frac{\text{Lag}}{\text{Range}}$.	Speed. r.p.m.
143	5	·01	7·2
144	88	·17	13·8
145	69	·14	21·0
146	40	·08	26·5
147	81	·16	32·9
148	36	·07	55·0

Fig. 13.



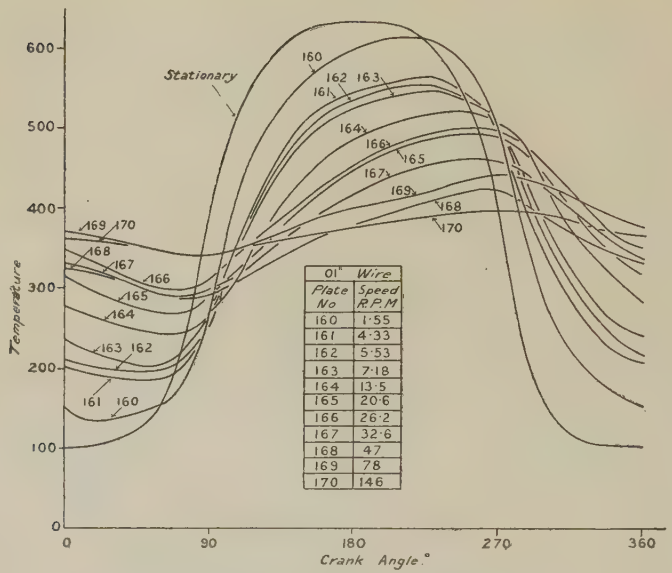
Experimental Curves, ·001 in. measuring wire.

·001 in. Wire.

Temperature Range 520° C.

Plate. No.	Lag. ° C.	Lag / Range.	Speed. r.p.m.
153	12	·02	6·5
154	36	·07	13·0
155	12	·02	19·8
156	28	·05	25·5
157	22	·04	32·3
158	22	·04	44·8

Fig. 14.



·01" Wire	
Plate No	Speed R.P.M
160	1·55
161	4·33
162	5·53
163	7·18
164	13·5
165	20·6
166	26·2
167	32·6
168	47
169	78
170	146

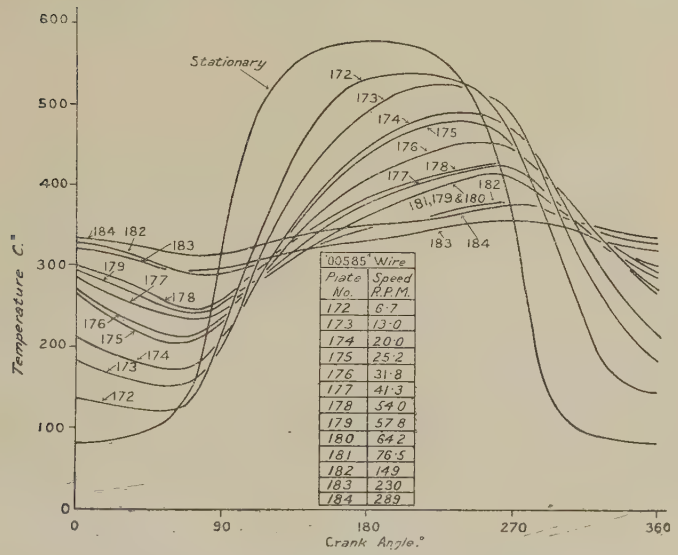
Experimental Curves, ·01 in. measuring wire.

·01 in. Wire.

Temperature Range 530° C.

Plate. No.	Lag. ° C.	$\frac{\text{Lag}}{\text{Range}}$.	Speed. r.p.m.
160	30	·057	1·5
161	87	·164	4·3
162	95	·179	5·5
163	108	·204	7·2
164	145	·274	13·5
165	180	·340	20·6
166	178	·335	26·2
167	210	·396	32·6
168	250	·470	47
169	230	·435	78
170	255	·480	146

Fig. 15.



Experimental Curves, ·00585 in. measuring wire.

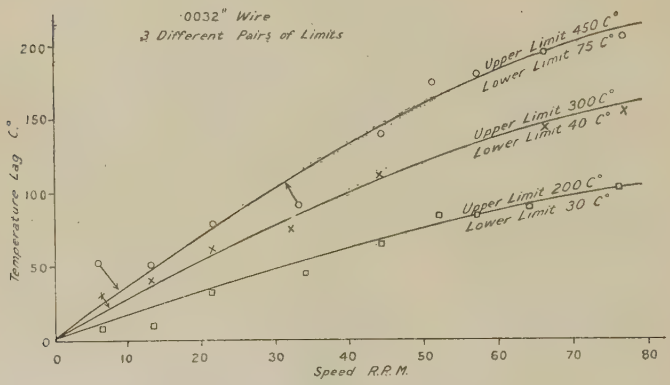
·C0585 in. Wire.

Temperature Range 495° C.

Plate. No.	Lag. ° C.	Lag / Range.	Speed. r.p.m.
172	47	·081	6·7
173	83	·143	13·0
174	130	·224	20·0
175	135	·233	25·2
176	170	·293	31·8
177	198	·342	41·3
178	193	·333	54·0
179	211	·364	57·8
180	215	·371	64·2
181	208	·359	76·5
182	230	·397	149
183	245	·423	230
184	228	·393	289

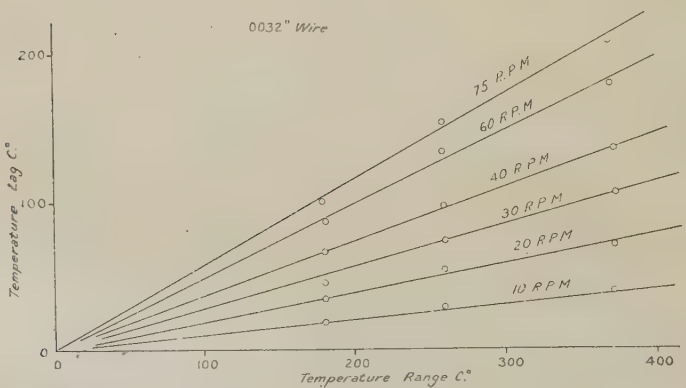
This is plotted in fig. 16 against speed for one diameter of wire (·0032 in.) and three different temperature ranges (370°, 260°, and 180° C.).

Fig. 16.



Curve showing Temperature Lag against Speed for the ·0032 in. measuring wire.

Fig. 17.

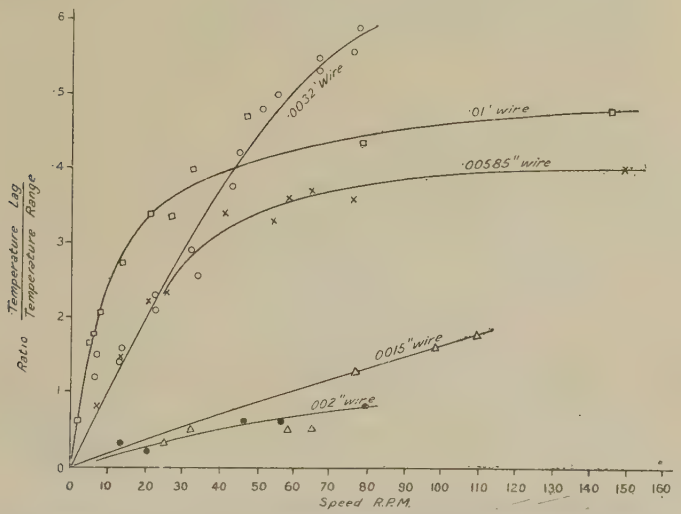


Curve showing Temperature Lag against Temperature Range for the ·0032 in. measuring wire.

Fig. 17 shows lag against range for the ·0032 in. wire at speeds of 10, 20, 30, 40, 60, and 75 r.p.m. This diagram is constructed from fig. 16. It will be noticed that at all

speeds the ratio of the lag to the range appears to be constant.

Fig. 18.



Curve showing Ratio of Temperature Lag to Temperature Range against Speed for all diameters of measuring wire used.

Assuming this to be true for all diameters of measuring wire, fig. 18 shows the ratio of temperature lag to temperature range against speed for all the diameters of wire used.

It is seen that for low speeds, the temperature lag is nearly proportional to the speed, but at higher speeds it approaches a limit.

The results of the first test on the ·001 in. wire were so inconsistent with each other that a second test was carried out, but the results were no better and could not be plotted in fig. 18.

It will be noticed that in successive tests the upper limit of stationary temperature increased, whereas the lower limit remained more or less constant. The shape of the stationary temperature distribution curve also gradually changed, commencing with a flat base and becoming more and more nearly symmetrical. This is taken to be due to the drying of the lagging material which was put round the heating element.

For this reason, the results obtained with the different diameters of wire are not comparable with each other, and it is not possible to draw any conclusions as to how the lag depends on the diameter of the measuring wire.

However, sufficient work has been done to show that, at atmospheric pressure and with comparatively quiescent air, the platinum resistance thermometer is not capable of following with sufficient accuracy temperature changes which take place with the rapidity which obtains in a gas-engine cycle.

It is anticipated that the conditions obtaining in the gas engine cylinder are much more favourable to thermometry on account both of the higher pressures existing and also of the turbulence, and experiments are now being conducted on a gas engine type of apparatus to determine whether this is the case.

Conclusion.

The whole of the casting, forging, and machining, besides most of the pattern making required in the construction of the apparatus have been carried out in the Mechanical Engineering Department of the University of Birmingham, and a considerable amount of the authors' time was taken up with this work.

The thanks of the authors are due to the members of the staff of the Workshops of the Department for assistance and facilities given in connexion with the work.

LVII. *Magnetic Rotary Dispersion in Gases.* *By* T. H. Havelock, *F.R.S.**

1. In studying the possible influence of anisotropy of the molecule on expressions for the dispersion of magnetic rotation in gases, it appeared that little comparison had been made with observations on the commoner gases such as hydrogen, nitrogen, and oxygen in regions free from absorption. In fact there are not many available results, as experimental work on gases has been chiefly concerned with the relatively large rotations in the neighbourhood of absorption.

In the following notes the point of view is the connexion between ordinary dispersion and that of magnetic rotation, and the comparison with experimental results; the survey covers briefly the various types of formulæ which have been used for the ordinary dispersion of a simple gas. In the first place, a single-term formula for an isotropic static molecule is compared with Siertsema's observations

* Communicated by the Author.

in the visible spectrum. The theory is then extended to an anisotropic static molecule, and the corresponding formulæ deduced; various cases are compared numerically with Sirks' values of the rotation in the ultra-violet. Finally, a similar study is made of the Bohr molecule for hydrogen, following the analysis developed by Sommerfeld and others.

Isotropic Static Molecule.

2. Assume the gas to consist of similar isotropic molecules, each containing a single elastically-bound vibrator of given charge and mass; and suppose further that the refractive index differs little from unity. Then, in the usual notation, the dispersion formula is

$$n^2-1=\frac{4\pi Ne^2}{m}\frac{1}{p_0^2-p^2}=\frac{Ne^2}{\pi c^2 m}\frac{1}{\lambda_0^{-2}-\lambda^{-2}}. \quad . \quad (1)$$

The corresponding expression for Verdet's constant for the magnetic rotation is

$$V=\frac{2\pi Ne^3p^2}{c^2m^2}\frac{1}{(p_0^2-p^2)^2}=\frac{Ne^3}{2\pi c^4m^2\lambda^2}\frac{1}{(\lambda_0^{-2}-\lambda^{-2})^2}. \quad . \quad (2)$$

Further, in this simple case, we have the equivalent expressions:

$$V=\frac{e\lambda}{2c^2m}\frac{dn}{d\lambda}=\frac{\pi}{2Ne\lambda^2}(n^2-1)^2. \quad . \quad . \quad . \quad . \quad (3)$$

Extensions of the formulæ have followed the usual course in the theory of dispersion: firstly by having on the left of (1) the quantity $(n^2-1)/(n^2+2)$ with the corresponding changes in (2) and (3), and secondly by a summation of terms on the right of (1) and (2) to include several natural periods of vibration. The latter extension has chiefly been made in applying a semi-empirical formula like

$$V\lambda^2=\frac{a_1}{(\lambda_2^{-2}-\lambda^{-2})^2}+\frac{a_2}{(\lambda_2^{-2}-\lambda^{-2})^2} \quad . \quad . \quad . \quad (4)$$

to liquids; in such cases, λ_1 and λ_2 are taken to be the natural wave-lengths of the corresponding dispersion formula, while a_1 and a_2, which are associated with the Zeeman coefficients for these lines, are left to be determined from experimental values of the magnetic rotation.

For gases when there is no absorption the rotation is

small, and this probably accounts for the lack of results obtained under ordinary conditions and extending over any considerable range of wave-length. Apart from the early work of Becquerel and others, there appear to be only two sets of experimental results. We shall consider first those obtained by Siertsema*. The observations were made with the gases under varying high pressures, and were reduced to uniform conditions under the assumption that the rotation is proportional to the density.

3. In Table I. column 2 shows Siertsema's values of Verdet's constant for hydrogen at 9°·5 C. and a pressure of 85 kg./cm.²; the rotations are in minutes and have been multiplied by 10^6, and the wave-lengths are in $\mu\mu$. Column 3 shows the relative values of $V\lambda^2$, which is the suitable quantity for which to form a dispersion formula; the departure from Biot's law is slight, but regular.

TABLE I.—Hydrogen.

λ.	V×10⁶.	Vλ².	From (6).
656	365	1·00	1·00
619	412	1·005	1·004
589	456	1·007	1·008
555	517	1·014	1·014
527	576	1·018	1·019
517	600	1·021	1·021
486	684	1·029	1·029
454	791	1·038	1·038
431	884	1·045	1·047
423	921	1·049	1·050

Siertsema expressed his results by two empirical formulæ, one $a/\lambda+b/\lambda^3$ and the other $a/\lambda^2+b/\lambda^4$. We use now a formula of the type (2), where λ_0 is derived from a simple dispersion formula. If we take the Cuthbertsons' formula for hydrogen,

$$n^2-1=\frac{3\cdot76\times10^{-4}}{1\cdot378777-10^{-10}\lambda^{-2}}, \quad . \quad . \quad . \quad (5)$$

we have for the rotation

$$V\lambda^2=\frac{C}{(1\cdot378777-10^{-10}\lambda^{-2})^2}. \quad . \quad . \quad . \quad . \quad (6)$$

The value of λ_0 is 851·6 A.U. Column 4 in Table I. shows the relative values calculated from (6). The agreement is quite satisfactory; hence, as far as this range of

* Siertsema, *Arch. Néerland.* ii. p. 291 (1899)

wave-length is concerned, a single-term formula with the same natural period is sufficient for both dispersions.

In regard to absolute values, there are various possible interpretations. Comparing (1) and (2) with (5) and (6), we may, for instance, regard e and m as the two unknown quantities and thus determine their values for a simple equivalent vibrator which will fit both the ordinary and the rotary dispersion.

Reducing Siertsema's results to absolute measure, we find that at normal temperature and pressure the value of V at the wave-length 656 is $1{\cdot}335 \times 10^{-9}$. Hence, taking $N = 2{\cdot}70 \times 10^{19}$, we have from (5) and (6) $e^2/m = 3{\cdot}96 \times 10^8$ and $e^3/m^2 = 1{\cdot}99 \times 10^{26}$. From these, $e = 7{\cdot}9 \times 10^{-10}$ and $m = 1{\cdot}57 \times 10^{-27}$; both values are less than twice the accepted electronic values, but the ratio $e/m = 1{\cdot}68 \times 10^7$ e.m.u. The usual numerical analysis follows rather different lines. It is more customary to assume, say, the electronic value of e and deduce e/m or the number of valency electrons and so forth, from the various relations between (1) and (2).

4. For nitrogen, Siertsema's values are shown in Table II.; the second column gives V in minutes at 14° C. and 100 kg./cm.^{2}, and the third column the relative values of $V\lambda^2$.

TABLE II.—Nitrogen.

λ.	$V \times 10^6$.	$V\lambda^2$.	From (7).
656	439	1·00	1·00
619	495	1·004	1·003
589	548	1·006	1·006
555	620	1·011	1·011
527	691	1·016	1·015
517	719	1·017	1·017
486	818	1·023	1·023
454	946	1·030	1·030
431	1054	1·036	1·037
423	1097	1·039	1·039

The value of λ_0 found by the Cuthbertsons from ordinary dispersion is 725·0 A.U. Using this for the rotation, we obtain values of $V\lambda^2$ which rise too slowly. With unity at 656, the value at 517 is 1·015 and at 423 is 1·036; the differences are no doubt within experimental error, but they are systematic. The fact is that experimental dispersion formulæ for nitrogen do not show very concordant

results when only a single term is used; recent experiments * indicate a considerably higher equivalent value of λ_0 than that found by Cuthbertson. Further, it must be remembered that Siertsema's observations were made at high pressures. In this case, then, we take the relative experimental values of $V\lambda^2$ from Table II., at the wave-lengths 656 and 423, and calculate the value of λ_0; we obtain thus $\lambda_0 = 759{\cdot}7$, a rather higher value than the Cuthbertsons' result for ordinary dispersion. With this value, we have

$$V\lambda^2 = \frac{C}{(1{\cdot}73263 - 10^{-10}\lambda^{-2})^2}. \quad . \quad . \quad . \quad . \quad (7)$$

The calculated values are shown in column 4 of Table II.

5. We note incidentally the anomalous behaviour of oxygen, which is brought out clearly when we consider $V\lambda^2$ instead of V as is usually the case. Siertsema's values are given in Table III. for oxygen at 7° C. and 100 kg./cm.^{2}

Table III.—Oxygen.

λ.	$V \times 10^6$.	$V\lambda^2$.
656	484	1·00
619	523	0·962
589	559	0·931
555	604	0·893
527	646	0·861
517	663	0·851
486	721	0·818
454	799	0·791
431	875	0·781
423	908	0·780

The striking result, shown in the third column, is that $V\lambda^2$ decreases with decreasing wave-length. It is obvious that a single-term formula like (2) is useless in this case. It would be necessary to use an empirical two-term formula like (4), with one of the constants a_1 and a_2 positive and the other negative. It would be possible to represent the course of $V\lambda^2$ in this way, but the range is not sufficient to determine the four constants of such a formula; even if we include later observations by Sirks, which carry the range into the ultra-violet, the results are not sufficiently definite and concordant. In addition, there is no corresponding formula for the ordinary dispersion of oxygen with which to make comparison. The anomalous behaviour of oxygen

* Stoll, *Ann. der Phys.* No. 18 (1922).

may naturally be ascribed to the fact that the gas is paramagnetic; and the suggested occurrence of a term signifying negative rotation may be associated with the reverse action of inter-molecular magnetic fields. In fact, it would be necessary to take into account magnetic properties of the molecule in devising a model to cover such a case.

Anisotropic Static Molecule.

6. In extending the previous formulæ to the ultra-violet, we shall find that the calculated values fall short of the observed dispersion. We proceed to modify the formulæ by taking into account the anisotropy of the molecule—an extension which has already been made in the theory of ordinary dispersion and related phenomena.

The medium is supposed to be a gas, with the refractive index nearly unity, composed of similar molecules for which all orientations are equally probable. Each molecule contains a vibrator of charge e and mass m, whose equilibrium position may be taken as the origin O; let the principal axes of the molecule for small vibrations be $O(\xi, \eta, \zeta)$, and let $O(x, y, z)$ be fixed directions in space, where the direction-cosines of the two sets of axes are given by the scheme:

	ξ	η	ζ
x	α_1	α_2	α_3
y	β_1	β_2	β_3
z	γ_1	γ_2	γ_3

The external magnetic field H being along Oz, we have

$$(H_\xi, H_\eta, H_\zeta) = (\gamma_1, \gamma_2, \gamma_3)H,$$

and the equations of motion of the vibrator are

$$\left.\begin{aligned} m\ddot{\xi} + mp_1^2\xi &= e\left(E_\xi + \frac{1}{c}\dot{\eta}\gamma_3 H - \frac{1}{c}\dot{\zeta}\gamma_2 H\right), \\ m\ddot{\eta} + mp_2^2\eta &= e\left(E_\eta + \frac{1}{c}\dot{\zeta}\gamma_1 H - \frac{1}{c}\dot{\xi}\gamma_3 H\right), \\ m\ddot{\zeta} + mp_3^2\zeta &= e\left(E_\zeta + \frac{1}{c}\dot{\xi}\gamma_2 H - \frac{1}{c}\dot{\eta}\gamma_1 H\right) \end{aligned}\right\} \quad . \quad . \quad (8)$$

The two sets of components of electric force are connected by relations of the form

$$\mathrm{E}_\xi = \alpha_1\mathrm{E}_x + \beta_1\mathrm{E}_y + \gamma_1\mathrm{E}_z, \quad . \quad . \quad . \quad . \quad . \quad (9)$$

and the components of the displacement by equations like

$$x = \alpha_1\xi + \alpha_2\eta + \alpha_3\zeta. \quad . \quad . \quad . \quad . \quad . \quad (10)$$

Suppose the electric force to vary as e^{ipt} ; then, writing k for $ipe\mathrm{H}/cm$, and a_1 for $p_1^2 - p^2$, etc., the equations (8) give

$$\left.\begin{aligned} a_1\xi - k\gamma_3\eta + k\gamma_2\zeta &= (e/m)\mathrm{E}_\xi, \\ k\gamma_3\xi + a_2\eta - k\gamma_1\zeta &= (e/m)\mathrm{E}_\eta, \\ -k\gamma_2\xi + k\gamma_1\eta + a_3\zeta &= (e/m)\mathrm{E}_\zeta. \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad (11)$$

We require to find the mean electric moment of the molecules per unit volume : that is, the mean values of ex, ey, ez in terms of E_x, E_y, E_z for all possible orientations of the axes (ξ, η, ζ). The process consists in solving (11) for ξ, η, ζ, and using (9) and (10). Neglecting powers of k higher than the first, we obtain after reduction

$$\begin{aligned} ex = (e^2/ma_1a_2a_3)[&(\alpha_1^2a_2a_3 + \alpha_2^2a_3a_1 + \alpha_3^2a_1a_2)\mathrm{E}_x \\ &+ \{\alpha_1\beta_1a_2a_3 + \alpha_2\beta_2a_3a_1 + \alpha_3\beta_3a_1a_2 + k\gamma_1(\alpha_2\beta_3 - \alpha_3\beta_2)a_1 \\ &\quad + k\gamma_2(\alpha_3\beta_1 - \alpha_1\beta_3)a_2 + k\gamma_3(\alpha_1\beta_2 - \alpha_2\beta_1)a_3\}\mathrm{E}_y \\ &+ \{\alpha_1\gamma_1a_2a_3 + \alpha_2\gamma_2a_3a_1 + \alpha_3\gamma_3a_1a_2 + k\gamma_1(\alpha_2\gamma_3 - \alpha_3\gamma_2)a_1 \\ &\quad + k\gamma_2(\alpha_3\gamma_1 - \alpha_1\gamma_3)a_2 + k\gamma_3(\alpha_1\gamma_2 - \alpha_2\gamma_1)a_3\}\mathrm{E}_z], \end{aligned} \quad (12)$$

with similar expressions for ey and ez.

The mean values may be found by expressing the direction-cosines in terms of Eulerian angles θ, ϕ, ψ, and taking the average for all possible values. We have

$$\overline{\alpha_1^2} = \ldots\ldots = \tfrac{1}{3} \; ; \quad \overline{\alpha_1\beta_1} = \ldots\ldots = 0 \; ;$$

$$\overline{\gamma_1(\alpha_2\beta_3 - \alpha_3\beta_2)} = \overline{\gamma_2(\alpha_3\beta_1 - \alpha_1\beta_3)} = \tfrac{1}{3} \; ; \quad \overline{\gamma_1(\alpha_2\gamma_3 - \alpha_3\gamma_2)} = 0$$

If N is the number of molecules per unit volume, we obtain finally for the components of mean polarization :

$$\left.\begin{aligned} \mathrm{P}_x &= \frac{\mathrm{N}e^2}{3m}\frac{1}{a_1a_2a_3}\left(\mathrm{E}_x\Sigma a_2a_3 + \frac{ipe\mathrm{H}}{cm}\mathrm{E}_y\Sigma a_1\right), \\ \mathrm{P}_y &= \frac{\mathrm{N}e^2}{3m}\frac{1}{a_1a_2a_3}\left(-\frac{ip\mathrm{H}}{cm}\mathrm{E}_x\Sigma a_1 + \mathrm{E}_y\Sigma a_2a_3\right), \\ \mathrm{P}_z &= \frac{\mathrm{N}e^2}{3m}\frac{1}{a_1a_2a_3}\mathrm{E}_z\Sigma a_2a_3. \end{aligned}\right\} \quad (13)$$

The refractive index is derived from the relation

$$P/E = (n^2-1)/4\pi ;$$

we neglect the influence of neighbouring molecules on the force acting on a vibrator.

In the absence of an external magnetic field, the aggregate behaves like an isotropic medium of refractive index given by

$$n^2-1 = \frac{4\pi Ne^2}{m}\left(\frac{1}{p_1^2-p^2}+\frac{1}{p_2^2-p^2}+\frac{1}{p_3^2-p^2}\right). \quad . \quad (14)$$

With a magnetic field H, parallel to Oz, we have from (13) the usual analysis for waves travelling along Oz; forming $P_x \pm iP_y$, we obtain the refractive indices for right and left circularly polarized waves :

$$n_\pm^2-1 = \frac{4\pi Ne^2}{m}\left(\Sigma\frac{1}{a_1} \mp \frac{pe\mathrm{H}}{cm}\Sigma\frac{1}{a_2a_3}\right). \quad . \quad . \quad (15)$$

Since Verdet's constant is equal to $p(n_- - n_+)/2c\mathrm{H}$, we obtain, with the assumption that n is nearly unity,

$$V = \frac{2\pi Ne^3p^2}{3c^2m^2}\left\{\frac{1}{(p_2^2-p^2)(p_3^2-p^2)}+\frac{1}{(p_3^2-p^2)(p_1^2-p^2)} + \frac{1}{(p_1^2-p^2)(p_2^2-p^2)}\right\}. \quad . \quad (16)$$

These are the direct generalizations of (1) and (2) for an isotropic molecule. It will be noticed that we do not have now formulæ like (3), such as Becquerel's relation ; V cannot be expressed directly in terms of n.

If the molecule has an axis of symmetry, so that $p_3=p_2$, we have

$$n^2-1 = \frac{4\pi Ne^2}{3m}\left(\frac{1}{p_1^2-p^2}+\frac{2}{p_2^2-p^2}\right), \quad . \quad . \quad . \quad . \quad . \quad (17)$$

$$V = \frac{2\pi Ne^3p^2}{3c^2m^2}\left\{\frac{1}{(p_2^2-p^2)^2}+\frac{2}{(p_1^2-p^2)(p_2^2-p^2)}\right\}. \quad (18)$$

We may put these into a form suitable for comparison later with Sommerfeld's formulæ for the Bohr molecule. If

we write $g=1/(p_1^2-p^2)$ and $g'=1/(p_2^2-p^2)$, we have

$$n^2-1=\frac{4\pi Ne^2}{3m}(g+2g'), \quad . \quad . \quad . \quad . \quad . \quad . \quad (19)$$

$$V=\frac{2\pi Ne^2p^2}{3c^2m^2}\left(2gg'+\frac{1}{2p}\frac{dg'}{dp}\right). \quad . \quad . \quad . \quad (20)$$

The influence of asymmetry of the molecule upon magnetic rotation has previously been studied by Gans *, who gives a result of the form

$$V\lambda^2=\text{const.}\left(\frac{1}{g}+\frac{2}{g'}\right)^{-2}=\frac{\text{const.}}{\{\frac{1}{3}(p_1^2+2p_2^2)-p^2\}^2}. \quad (21)$$

This appears to have been obtained by an incorrect method of finding the mean polarization for all possible orientations. Using data for the asymmetry derived from the polarization of scattered light, Gans applies his formulæ to Siertsema's experiments. But we have seen that these are quite well fitted by a simple formula, and we shall see that in this range the difference between formulæ (2) and (18) is quite inappreciable compared with possible experimental error; therefore information about the asymmetry of the molecule cannot be derived from magnetic rotation without observations of greater accuracy or covering a greater range of wave-length.

7. Before discussing numerical results, we may consider briefly the case of a paramagnetic molecule with an intrinsic magnetic moment M. There is now an orientation of the molecule in the magnetic field, so that in averaging the electric moment all orientations are not equally probable. If we assume the magnetic axis to be the axis $O\zeta$, the distribution function is

$$e^{MH\gamma_3/kT},$$

where k is the gas constant and T the absolute temperature.

Thus, assuming MH/kT to be small, we must multiply the previous expressions (12) for the electric moment by $1+MH\gamma_3/kT$ and then take mean values as before. It can easily be verified that the additional terms of the first order in H so obtained do not give any final contribution to the value of the mean polarization. On this theory the orientation of paramagnetic molecules only introduces terms of order

* R. Gans, *Ann. der Phys.* lxv. p. 119 (1921).

higher than the first. This statement applies to a molecule in which the electric charges vibrate about positions of equilibrium. It is otherwise for a molecule, such as the Bohr model, in which the vibrations are about a steady state of rotation ; then orientation affects the magnetic rotation with terms of the first order in H.

8. We turn now to comparison with experiment. Siertsema's work has been extended by Sirks *, whose relative values of V for hydrogen are shown in Table IV. ; the corresponding relative values of $V\lambda^2$ are given in the third column.

TABLE IV.—Hydrogen.

λ.	V.	$V\lambda^2$.
578	1·00	1·00
546	1·125	1·003
486	1·44	1·018
436	1·815	1·033
404	2·15	1·054
366	2·64	1·061
313	3·90	1·144
280	5·14	1·210
265	5·975	1·261
253	6·67	1·283
248	7·09	1·305
240	7·76	1·338
238	7·94	1·346

In the first place, $V\lambda^2$ has been calculated for a few wavelengths from the formula (6) ; these are shown in Table V. The values fall short considerably in the ultra-violet.

I have shown previously † that the ordinary dispersion of hydrogen can be represented by two formulæ of the type (17) over the range 5462 to 1854 A.U. ; and that these formulæ also give reasonable agreement with observations on the polarization of scattered light. They are

$$n^2-1 = 1{\cdot}242958\times10^{-4}\left\{\frac{1}{1{\cdot}032551-10^{-10}\lambda^{-2}} + \frac{2}{1{\cdot}638331-10^{-10}\lambda^{-2}}\right\} \quad (22)$$

* J. F. Sirks, *Phys. Zeit.* xiv. p. 336 (1913).
† Proc. Roy. Soc. A, ci. p. 154 (1922).

and

$$n^2-1 = 1{\cdot}2429583\times10^{-4}\left\{\frac{1}{2{\cdot}088392-10^{-10}\lambda^{-2}} + \frac{2}{1{\cdot}169513-10^{-10}\lambda^{-2}}\right\}. \quad (23)$$

From (18) the corresponding formulæ for $V\lambda^2$ are

$$V\lambda^2 = \frac{C}{(1{\cdot}6383-x)}\left\{\frac{1}{1{\cdot}6383-x}+\frac{2}{1{\cdot}0325-x}\right\}, \quad (24)$$

and

$$V\lambda^2 = \frac{C}{(1{\cdot}1695-x)}\left\{\frac{1}{1{\cdot}1695-x}+\frac{2}{2{\cdot}0884-x}\right\}, \quad (25)$$

where x has been put for $10^{-10}\lambda^{-2}$.

The calculated values are shown in the third and fourth columns of Table V.

Table V.—Calculated $V\lambda^2$.

λ.	(6)	(24)	(25)	(27)
578	1·00	1·00	1·00	1·00
436	1·034	1·035	1·037	1·030
280	1·161	1·167	1·171	1·139
248	1·230	1·239	1·245	1·201
238	1·259	1·270	1·275	1·227

The values are better than those from (6), but they still fall much short of Sirks' values in the smaller wave-lengths. There are various reasons for not accepting the comparison as conclusive, but taking it as it stands it would seem that the model of (22) and (23) does not include fully the dispersion of magnetic rotation. Comparing (22) and (23) with (17), we find that if e and m have their electronic values, and if there are two electrons per molecule, then the constant 1·243 in (22) and (23) should have been 1·606; the smaller value denotes coupling between the two electrons. There is perhaps no reason to expect that the magnetic rotation should be expressed accurately by the same equivalent vibrator as for ordinary dispersion or other electrical effects. This suggests trying a dispersion formula

for hydrogen in which the constant has the accepted electronic value. One of this character has been given by Lundblad*; it was obtained by regarding the molecule as made up of two interacting doublets. When put into partial fractions and expressed in wave-lengths, it becomes

$$\frac{n^2-1}{n^2+2}=\frac{1{\cdot}605896\times10^{-4}}{3}\left\{\frac{1}{0{\cdot}976725-10^{-10}\lambda^{-2}}+\frac{2}{2{\cdot}977210-10^{-10}\lambda^{-2}}\right\}. \quad (26)$$

This formula fits the ordinary dispersion well in the range 546 to 230, but, as I have shown previously, it does not agree with observations on the polarization of scattered light. Treating it as of type (17), the corresponding magnetic rotation should be

$$V\lambda^2=\frac{C}{(2{\cdot}9772-x)}\left\{\frac{1}{2{\cdot}9772-x}+\frac{2}{0{\cdot}9767-x}\right\}. \quad (27)$$

Calculated values are shown in the last column of Table V.; the agreement with observation is much worse than for (22) and (23).

But it is quite possible that the experimental results are not suitable for elaborate analysis. It should be remarked that the dispersion formulæ (22) and (23) were derived from the dispersion of hydrogen under usual conditions, while for the magnetic rotation the gas was under a pressure of 70–90 atmospheres; further, different samples of gas gave rather different results. It may be that the ordinary dispersion was different under these conditions; in fact, Sirks, in attempting to deduce e/m from his results by a formula like (1) or (2), assumes the natural wave-length λ_0 to be 870, which is appreciably higher than the value 851 of Cuthbertson's formula (5) or than the mean in either (22) or (23). Further, this difference is in the right direction for accounting for the discrepancy. This opinion is confirmed if we use the Becquerel formula (3) and calculate $V\lambda^2$ as proportional to $\lambda^3 dn/d\lambda$. Seeing that (22) and (23) represent the dispersion of hydrogen with great accuracy, this is equivalent to calculating $V\lambda^2$ from a formula of the

* Lundblad, *Untersuch. über die Optik*, p. 192 (1920).

type (4), in which the natural vibrations specified by λ_1 and λ_2 are treated as due to independent vibrators with the same Zeeman coefficient. The calculation gives the ratio 1·3 for the extreme wave-lengths instead of the observed value 1·346, and it seems that any modification like (24) or (25) should give a less value than 1·3. Before attempting any further analysis, it would be desirable to have parallel sets of observations of ordinary and rotary dispersion carried out, if possible, on the same gas under similar conditions.

Bohr Hydrogen Molecule.

9. To complete this survey it is of interest to make the same comparison for the Bohr molecule, as an example of vibrations about steady motion, in contrast to the previous static molecules. It is not our intention to criticize the defects of the original Bohr model, or the foundations of the dispersion theory: for the latter, one may refer to a recent critical study by Epstein *. The theory of dispersion and of magnetic rotation has been developed by Sommerfeld † and by Pauer ‡, from whose work we quote the results necessary to illustrate the points in question, making some slight changes in notation.

Using the notation of § 6, with $O\zeta$ as the line joining the two nuclei of the molecule, the components of electric moment of the molecule in the absence of any external magnetic field are given by

$$\left.\begin{aligned} P_\xi &= -\frac{e^2}{mp_0^2}\left[\{f(x)+f(-x)\}E_\xi + i\{f(x)-f(-x)\}E_\eta\right], \\ P_\eta &= -\frac{e^2}{mp_0^2}\left[\{f(x)+f(-x)\}E_\eta - i\{f(x)-f(-x)\}E_\xi\right], \\ P_\zeta &= -\frac{2e^2}{mp_0^2}\phi(x)E_\zeta, \end{aligned}\right\} \quad . \quad . \quad . \quad (28)$$

where $x = p/p_0$.

Here p_0 is the angular velocity of the two ring-electrons in the steady state, and is determined by applying the

* P. S. Epstein, *Zeit. für Phys.* ix. p. 92 (1922).
† A. Sommerfeld, *Ann. der Phys.* liii. p. 497 (1917).
‡ F. Pauer, *Ann. der Phys.* lvi. p. 261 (1918).

quantum rule to each electron ; the numerical value so found is $4{\cdot}55 \times 10^{16}$.

The small vibrations about the steady state are assumed to follow the ordinary laws of dynamics, and the functions f and ϕ in (28) are found in this way from the equations of motion of the ring-electrons for forced vibrations of frequency p. It may be noted that the molecule, so defined, is dynamically unstable. For hydrogen,

$$\left.\begin{aligned} f(x) &= \frac{(x-2)^2+0{\cdot}15479}{(x-1)^4-1{\cdot}69042(x-1)^2-0{\cdot}607197}, \\ \phi(x) &= \frac{1}{x^2-0{\cdot}30958}. \end{aligned}\right\} \quad (29)$$

With all orientations of the molecule equally probable, the refractive index follows from (28) by the usual method of averaging, with the result

$$n^2-1 = -\frac{8\pi Ne^2}{3mp_0^2}\{f(x)+f(-x)+\phi(x)\}, \quad . \quad . \quad (30)$$

where e and m are the charge and mass of a single electron.

When there is an external magnetic field, the application of the quantum rule is a point that requires further investigation. For various reasons, Sommerfeld and Pauer in their analysis use the rule as determining the steady state only in the absence of a magnetic field. The small vibrations are determined from the equations of motion. Apart from the form of the functions f and ϕ, the analysis proceeds on similar lines to that for a static molecule ; the resulting expression for Verdet's constant for hydrogen is

$$V = \frac{4\pi Ne^3}{3c^2m^2}\,\frac{p}{p_0^3}\left[x\phi(x)\{f(x)+f(-x)\}-\tfrac{1}{4}\{f'(x)-f'(-x)\}\right]. \quad . \quad . \quad . \quad (31)$$

The functions ϕ and f are associated with axial vibrations and those in the plane of the ring respectively ; if we put

$$g = -\phi(x)/p_0^2\,; \quad g' = -\{f(x)+f(-x)\}/2p_0^2, \quad . \quad (32)$$

then g and g' correspond to the same quantities as in § 6.

Equation (30) is now

$$n^2-1=\frac{8\pi \mathrm{N}e^2}{3m}(g+2g'), \quad . \quad . \quad . \quad . \quad (33)$$

and (31) reduces to

$$\mathrm{V}=\frac{4\pi \mathrm{N}e^2p^2}{3c^2m^2}\left(2gg'+\frac{1}{2p}\frac{dg'}{dp}\right). \quad . \quad . \quad . \quad (34)$$

These results are of the same form as (19) and (20) for the static molecule, as might have been expected, since the quantum rule was only used to define the steady state.

10. There is, however, a notable difference between the two cases if the medium is paramagnetic. Here again, as in § 7, we have to multiply the expressions for the electric polarization by $1+\mathrm{M}\mathrm{H}\gamma_3/k\mathrm{T}$, before taking mean values. But there remain now terms of the first order; Sommerfeld's expression for Verdet's constant is (31) with an additional term within the square brackets, namely

$$(mc\mathrm{M}/2ke\mathrm{T})\{f(x)-f(-x)\}. \quad . \quad . \quad . \quad . \quad (35)$$

Numerical calculation shows that for oxygen this new term is many times greater than the other terms of (31); in fact, the same remark would hold for the Bohr hydrogen molecule. Sommerfeld avoids the difficulty by concluding that paramagnetism is atomic and not molecular, so that orientation does not affect directly the orbits which are under consideration in the theory of dispersion.

It is obvious that the difference from the static molecule arises from the fact that the medium would have intrinsic rotational properties if the molecules were not orientated at random. If, for instance, we imagine the axes of the molecules to be all in the same direction, without considering any other effects that might be produced, it follows from (28) that the medium would be rotational with a gyric coefficient

$$\frac{2\pi \mathrm{N}e^2p}{mcp_0^2}\left\{f\left(\frac{p}{p_0}\right)-f\left(-\frac{p}{p_0}\right)\right\}. \quad . \quad . \quad . \quad (36)$$

A numerical estimate for the hydrogen molecule shows that this would have an enormous value compared with actual rotational coefficients.

11. For comparison with experimental results, Sommerfeld expanded (30) and (31) in powers of x and used the first

two terms of the expansion in each case ; it was found that the values agreed fairly well with the ordinary dispersion, and also with Siertsema's results for magnetic rotation, provided p_0 was taken as $4{\cdot}51 \times 10^{16}$ instead of the supposed quantum value $4{\cdot}55 \times 10^{16}$.

The calculations are now extended to the ultra-violet, using the exact formula (31) with $p_0 = 4{\cdot}51 \times 10^{16}$ and f and ϕ as in (29). The relative values of $V\lambda^2$ are shown in the second column of Table VI., and may be compared with Sirks' results given in Table IV.

For absolute values we take the wave-length 656. We saw in § 3 that Siertsema's value for V is $1{\cdot}335 \times 10^{-9}$; the formula (31) gives $1{\cdot}2 \times 10^{-9}$.

The comparison between the formula (30) and ordinary dispersion has been extended recently to the ultra-violet by Gans *, using the experimental values of Kirn. Gans finds that the dispersion, apart from absolute values, is fitted more accurately by taking $p_0 = 4{\cdot}3 \times 10^{16}$. Calculating now the magnetic rotation from (31) with this value of p_0, we find the relative values of $V\lambda^2$ as given in the third column of Table VI.

TABLE VI.—Values of $V\lambda^2$.

λ.	$p = 4{\cdot}51$.	$p_0 = 4{\cdot}3$.
578	1·00	1·00
436	1·033	1·036
280	1·183	1·206
238	1·297	1·336

The new value of p_0 gives a better agreement with Sirks' results for the relative rotary dispersion ; but this has been obtained by some sacrifice as regards absolute values both for the ordinary and the rotary dispersion. With the accepted values of N, e, and m, and with $p_0 = 4{\cdot}3 \times 10^{16}$, the values of $n^2 - 1$ from (30) are about 10 per cent. greater than Kirn's experimental values ; further, the corresponding value of Verdet's constant at wave-length 656 is $1{\cdot}454 \times 10^{-9}$, which is larger than Siertsema's value. Another way of expressing the divergence is by calculating $dn/d\lambda$ from (30) or (33) ; the ratio of $\lambda^3 dn/d\lambda$ at the wave-lengths 238 and

* R. Gans, *Zeit. für Phys.* ix. p. 81 (1922).

578 is found to be 1·378, which is considerably higher than the value 1·3 obtained in § 8 from Kirn's results. In any case it appears that, in order to make (30) and (31) agree with observed results, it is necessary to treat them as formulæ with two or three disposable constants; the theory then loses its value as one giving results directly in terms of known electronic constants.

Summary.

12. A comparison is made between the ordinary dispersion of certain gases and the dispersion of magnetic rotation in regions free from absorption. It is shown that formulæ derived from a simple static molecule with one type of vibrator are sufficient for both dispersions in the visible spectrum for gases like hydrogen and nitrogen. On the other hand, the case of oxygen, in which $V\lambda^2$ decreases with decreasing wave-length, indicates the necessity of including the magnetic properties of the molecule before a complete theory can be formed.

Omitting paramagnetic effects, expressions for the rotary dispersion are obtained for an anisotropic static molecule, such as has been used for the ordinary dispersion of hydrogen. Two formulæ of this kind are compared with Sirks' observations in the ultra-violet; the modification improves the agreement, but not to a sufficient extent.

Similar conclusions are reached after a numerical study of the Bohr molecule for hydrogen, following Sommerfeld's analysis of the ordinary and magnetic dispersion.

It is pointed out that in all cases the adjustable constants of the ordinary dispersion formulæ were found by comparison with experiments on gases under ordinary conditions of temperature and pressure; while the available data for magnetic rotation were obtained from gases under high pressures. It may well be the case that the results are not strictly comparable; and it is desirable that parallel sets of observations should be made on the same gas under similar conditions.

LVIII. *The Sum of Series of Cosecants.* *By* G. N. Watson, *Sc.D., F.R.S., Professor of Mathematics in the University of Birmingham* *.

1. In a paper on Atomic Systems recently published in this Magazine by Mr. R. Hargreaves †, the series

$$S_n^{(1)} \equiv \sum_{m=1}^{n-1} \operatorname{cosec} \frac{m\pi}{n}, \qquad S_n^{(3)} \equiv \sum_{m=1}^{n-1} \operatorname{cosec}^3 \frac{m\pi}{n},$$

where n is a large integer, were encountered in the course of the analysis. I have already published ‡ an investigation of the asymptotic expansion of the former, with a table of numerical values, and, in view of the interest aroused in the latter by Mr. Hargeaves's researches, I propose to investigate it by the same methods. I must admit that my methods are of a slightly more recondite nature than the elementary methods used by Mr. Hargreaves; but, to compensate for this, they give complete asymptotic expansions, and, moreover, they indicate the nature of the asymptotic expansion when any odd powers of the cosecants, other than the first and third, are involved.

The result contained in my former paper was

$$\pi S_n^{(1)} \sim 2n \log_e (2n) + 2n(\gamma - \log_e \pi) + 2 \sum_{m=1}^{\infty} \frac{(-)^m B_m {}^2 \pi^{2m} (2^{2m-1} - 1)}{m \,.\, (2m)!\, n^{2m-1}}.$$

In this formula, γ is Euler's constant, B_1, B_2, B_3, ... are the numbers of Bernoulli, while the error due to stopping at any term of the series is of the same sign as, and numerically less than, the first term neglected.

2. To investigate $S_n^{(3)}$ we twice differentiate Euler's formula

$$\int_0^\infty \frac{x^{a-1} dx}{1+x} = \frac{\pi}{\sin a\pi}, \qquad (0 < a < 1)$$

with respect to a, and get

$$\int_0^\infty \frac{(\log x)^2 x^{a-1} dx}{1+x} = \frac{\pi^3}{\sin^3 a\pi} (2 - \sin^2 a\pi).$$

* Communicated by the Author.
† Phil. Mag. (6) vol. xliv. pp. 1065–1105 (1922).
‡ Phil. Mag. (6) vol. xxxi. pp. 111–118 (1916).

It follows at once that

$$2\pi^3 S_n^{(3)} - \pi^3 S_n^{(1)} = \int_0^\infty \frac{(\log x)^2}{x(1+x)} \{x^{1/n} + x^{2/n} + \ldots + x^{(n-1)/n}\}\, dx$$

$$= \int_0^\infty \frac{(\log x)^2 (x^{1/n} - x)\, dx}{x(1+x)(1-x^{1/n})}$$

$$= n^3 \int_0^\infty \frac{(\log y)^2 (1-y^{n-1})\, dy}{(1+y^n)(1-y)}$$

$$= n^3 \int_{-\infty}^\infty \frac{t^2 (1-e^{-(n-1)t})\, dt}{(1+e^{-nt})(e^t-1)}$$

$$= 2n^3 \int_0^\infty \frac{t^2 (1-e^{-(n-1)t})\, dt}{(1+e^{-nt})(e^t-1)},$$

when we sum the geometrical progression and then write $x^{1/n} = y = e^{-t}$; the final step, of bisecting the range of integration, is justified by the consideration that the integrand is an even function of t.

3. To obtain the asymptotic expansion of the last integral we proceed much as in my former paper, the analysis being simplified by the presence of the factor t^2 in the numerator.

We re-write the integrand thus:

$$\frac{t^2(1-e^{-(n-1)t})}{(1+e^{-nt})(e^t-1)} = \frac{t^2}{e^t-1} - \frac{2e^{-nt}}{1+e^{-nt}} \left\{\frac{t^2}{e^t-1} + \frac{t^2}{2}\right\},$$

and if, for brevity, we put

$$\frac{1}{1^m} + \frac{1}{2^m} + \frac{1}{3^m} + \ldots = \sigma_m,$$

we have

$$\int_0^\infty \frac{t^2\, dt}{e^t-1} = \sum_{r=1}^\infty \int_0^\infty t^2 e^{-rt}\, dt$$

$$= 2! \sum_{r=1}^\infty r^{-3}$$

$$= 2\sigma_3.$$

Again we have

$$\frac{t^2}{e^t-1} + \frac{t^2}{2} = t + \mathrm{B}_1 \frac{t^3}{2!} - \mathrm{B}_2 \frac{t^5}{4!} + \ldots + (-)^{r-1} \mathrm{B}_r \frac{t^{2r+1}}{(2r)!}$$

$$+ (-)^r \theta \mathrm{B}_{r+1} \frac{t^{2r+3}}{(2r+2)!},$$

where $0 \leq \theta \leq 1$; and so we get

$$2\pi^3 S_n^{(3)} - \pi^3 S_n^{(1)} = 4\sigma_3 n^3 - 4n^3 \int_0^\infty \frac{t\,dt}{e^{nt}+1}$$
$$+ 4n^3 \int_0^\infty \frac{dt}{e^{nt}+1} \left\{ \sum_{m=1}^{r} (-)^m B_m \frac{t^{2m+1}}{(2m)!} \right.$$
$$\left. + (-)^{r+1} \theta B_{r+1} \frac{t^{2r+3}}{(2r+2)!} \right\}.$$

When we make use of the formula

$$\int_0^\infty \frac{u^m\,du}{e^u+1} = m!\,(1-2^{-m})\sigma_{m+1},$$

which was established in my former paper, we find, on writing u in place of nt,

$$2\pi^3 S_n^{(3)} - \pi^3 S_n^{(1)} \sim 4\sigma_3 n^3 - 2n\sigma_2$$
$$+ 4 \sum_{m=1}^{\infty} \frac{(-)^m (2m+1) B_m (1-2^{-2m-1}) \sigma_{2m+2}}{n^{2m-1}},$$

the error due to stopping at any term being of the same sign as, and numerically less than, the first term neglected.

Replacing σ_{2m+2} by $2^{2m+1}\pi^{2m+2} B_{m+1}/(2m+2)!$, and substituting for $S_n^{(1)}$ the expansion quoted in § 1, we find that

$$\pi^3 S_n^{(3)} \sim 2\sigma_3 n^3 + \pi^2 n \log_e n + \pi^2 n (\gamma - \tfrac{1}{6} - \log_e \tfrac{1}{2}\pi)$$
$$+ \sum_{m=1}^{\infty} \frac{(-)^m B_m \pi^{2m+2}}{(2m)!\, n^{2m-1}} \left\{ \frac{2^{2m-1}-1}{m} B_m + \frac{2^{2m+1}-1}{m+1} B_{m+1} \right\},$$

the series possessing the usual property concerning the magnitude and sign of the remainder.

For purposes of tabulation this expansion may be written in the form

$$S_n^{(3)} = n^3 \times 0{\cdot}07753\ 63592\ 05833\ 59787$$
$$+ (n \log_{10} 2n) \times 0{\cdot}73293\ 55992 - n \times 0{\cdot}23369\ 70348$$
$$- n^{-1} \times 0{\cdot}07417\ 64932 + n^{-3} \times 0{\cdot}01561\ 93435$$
$$- n^{-5} \times 0{\cdot}01319\ 98 + n^{-7} \times 0{\cdot}04576.$$

From these numerical results, the following table was constructed, with the exception of the entries for $n = 2, 3, 4, 5,$

which were calculated directly and not from the asymptotic expansion :—

n.	$S_n^{(3)}$.	n.	$S_n^{(3)}$.
2	1·00000	25	1236·79111
3	3·07920	26	1389·40079
4	6·65685	27	1554·11838
5	12·17352	28	1731·40865
6	20·07920	29	1921·73639
7	30·82881	30	2125·56643
8	44·88014	35	3363·52172
9	62·69282	40	5008·77095
10	84·72770	45	7119·43774
11	111·44650	50	9753·65213
12	143·31156	55	12969·54859
13	180·78572	60	16825·26489
14	224·33215	65	21378·94118
15	274·41434	70	26688·71951
16	331·49599	75	32812·74338
17	396·04101	80	39809·15746
18	468·51343	85	47736·10739
19	549·37746	90	56651·73956
20	639·09736	95	66614·20104
21	738·13754	100	77681·63944
22	846·96244	360	3618206·17062
23	966·03660	1000	77538544·95112
24	1095·82461		

4. If the formula

$$\int_0^\infty \frac{x^{a-1}\,dx}{1+x} = \frac{\pi}{\sin a\pi}$$

is differentiated $2r$ times with respect to a (r being any assigned positive integer) it is easy to prove by the methods already used that the dominant term of the asymptotic expansion of

$$\sum_{m=0}^{n-1} \operatorname{cosec}^{2r+1} \frac{m\pi}{n}$$

is $\qquad 2\pi^{-2r-1}\sigma_{2r+1}\,n^{2r+1} \qquad (r \geqslant 1).$

In like manner it may be found from the formula

$$\mathrm{P}\int_0^\infty \frac{x^{a-1}\,dx}{1-x} = \frac{\pi}{\tan a\pi}$$

that the dominant term of the series for

$$\sum_{m=0}^{n-1} \operatorname{cosec}^{2r} \frac{m\pi}{n}$$

is $2\pi^{-2r}\sigma_{2r}n^{2r}$, which is equal to

$$(2n)^{2r}\mathrm{B}_r/(2r)!$$

But, since the values of $\operatorname{cosec}^2(m\pi/n)$, for acute values of $m\pi/n$, are the roots of the equations

$$x^{\frac{1}{2}n-1} - \frac{n^2-2^2}{3!}x^{\frac{1}{2}n-2} + \frac{(n^2-2^2)(n^2-4^2)}{5!}x^{\frac{1}{2}n-3} - \ldots = 0,$$

$$x^{\frac{1}{2}(n-1)} - \frac{n^2-1^2}{3!}x^{\frac{1}{2}(n-3)} + \frac{(n^2-1^2)(n^2-3^2)}{5!}x^{\frac{1}{2}(n-5)} - \ldots = 0,$$

(according as n is even or odd), it is evident that the series for

$$\sum_{m=0}^{n-1} \operatorname{cosec}^{2r}\frac{m\pi}{n}$$

terminates, and that it is a polynomial in n^2 of degree r in which the coefficients can be calculated with sufficient labour for any assigned value of r.

LIX. *A simple Form of Apparatus for observing the Rate of Reaction between Gases and Liquids, and its Use in determining the Rate of Solution of Oxygen by Water under Different Conditions of mixing.* *By* H. G. Becker, *A.R.C.Sc.I., A.I.C., Demonstrator in Chemistry, Royal College of Science, Dublin* *.

I. Introduction.

THE apparatus described in this paper was primarily devised as an alternative method of carrying out the "Five Days' Dissolved Oxygen Absorption Test," and is based on a principle previously utilized by Prof. Adeney for the same purpose †.

In the course of the work, however, it became apparent that the principle was capable of wider application, and the apparatus was finally designed with a view to its possible use for the study of gas-liquid systems in general.

The effect of different rates of stirring on the rate of solution of oxygen in water has been determined by means of the apparatus, and the results of the experiments are given in this communication, as they have a direct bearing on some previously published work ‡.

* Communicated by Prof. W. E. Adeney, A.R.C.Sc.I., D.Sc. Reprinted from the Proceedings of the Royal Dublin Society, vol. xvi. (n.s.).

† Fifth Report, Royal Commission on Sewage Disposal, Appendix vi. p. 438.

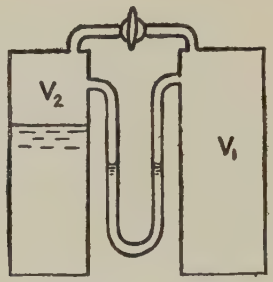
‡ Adeney and Becker, Scientific Proc. R. D. S. xv. p. 609 (1919).

II. The Principle on which the Apparatus is based.

The principle utilized in the apparatus depends on the changes in pressure which occur when a liquid is placed in contact with a closed volume of a gas which it is capable of absorbing, and the action of the apparatus will be understood by reference to fig. 1.

In the system shown in the diagram there is a volume of gas V_2 connected through a manometer with a volume of gas V_1, there being sufficient liquid in V_1 to ensure saturation of the gas with vapour, and the liquid under test is in contact with the gas in V_2. When the tap is closed, any absorption of gas by the liquid from V_2 results in a decrease in pressure, which is indicated on the manometer, and from

Fig. 1.



the manometer reading the volume of gas absorbed can be calculated. With such an arrangement it is possible to vary the sensitivity of the manometer considerably. The smaller the volume V_2 becomes in comparison with V_1, the greater the movement of the manometer (within limits) for a given absorption of gas by the liquid. Further, when the tap connecting V_2 and V_1 is opened the manometer returns to zero, and the difference in pressure previously existing in V_2 is distributed between the combined volume, thus making it a much smaller fraction of the whole. With such an arrangement it become possible to reset the manometer to zero several times during the course of an experiment, without allowing the pressure in V_2 to fall to such a value as would seriously affect the solubility of the gas. The tap also affords an easy method of replenishing the supply of one of the constituent gases of a mixture contained in V_2. Thus, if V_2 contains atmospheric air in contact with a liquid absorbing oxygen, and V_1 contains pure oxygen, then, after a given absorption, the opening of tap resets the manometer,

and also replaces the oxygen absorbed to an extent which will depend on the ratio $\frac{V_2}{V_1}$.

The conditions at the start of an experiment are such that the pressures in V_1 and V_2 are equal to each other and to the atmospheric pressure P mm.

Now, suppose an absorption of Q c.c. takes place in V_2, and that the resulting manometer reading is p mm., then (V_2-Q) c.c. at P are occupying (V_2-v_1) at P_x, where v_1 = the volume of liquid which has risen above the zero point in the manometer, and V_1 c.c. at P are occupying (V_1+v_1) c.c. at P_y.

Now, since $$P_y=P_x+p,$$

$$\therefore \quad \frac{PV_1}{V_1+v_1}=\frac{P(V_2-Q)}{V_2-v_1}+p,$$

which gives

$$Q=v_1\frac{(V_2+V_1)}{V_1+v_1}+\frac{p}{P}(V_2-v_1).$$

If the two vessels are now connected by opening the tap, P_y becomes equal to P_x, and $p=0$.

There is then $V_1+(V_2-Q)$ c.c. at P occupying a volume V_1+V_2 at P_z.

Hence $$P_z=\frac{P(V_1+V_2-Q)}{V_1+V_2}$$

$$=P\left(1-\frac{Q}{V_1+V_2}\right).$$

Hence the pressure in the air spaces after resetting the manometer will be less than that existing at the start by a quantity dependent on the ratio of the volume of gas absorbed to the combined volume of the two air spaces. By making the latter large this quantity can be made very small at will.

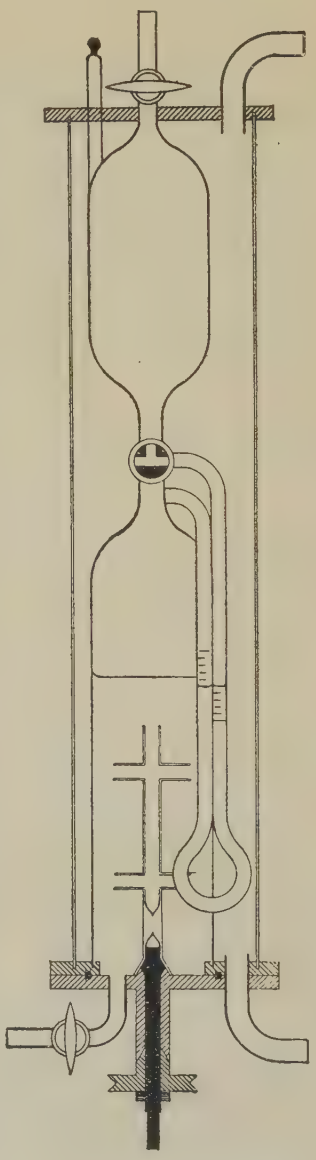
III. Description of Apparatus.

The apparatus which was devised on this principle is shown diagrammatically in fig. 2.

It consists of two cylindrical glass vessels about 30 mm. in diameter, which are connected to two branches of a three-way tap. The lower vessel is of such a size as to contain a suitable volume (say, 100 c.c.) of liquid to be tested, and still leave room for an air space of about 50 c.c.; the upper vessel also has a capacity of about 50 c.c. The three-way

tap allows of the two air spaces being connected through the manometer, or directly, according to its position. Hence, when an absorption has taken place, the manometer can be reset to zero by suitably turning the tap.

Fig. 2.



The whole apparatus, including the manometer, is enclosed in a cylindrical water-jacket, through which water is circulated from a thermostat. The handle of the three-way tap projects through a hole blown in this water jacket, the joint being kept water-tight by means of a rubber diaphragm. The water-jacket is closed at each end by flanges, which may be made of brass, tin, or ebonite, according to the purpose for which the apparatus is to be used.

The stirrer passes through a long sleeve in the lower flange, and is provided with two conical surfaces, one of which can be adjusted by means of a screw, so that the whole is water-tight. In addition, the glass part of the stirrer is expanded into a cone at the lower end, which is ground to fit a corresponding cone on the bearing, so that the metallic parts of the stirrer do not come into contact with the liquid at any point.

The glass part of the stirrer is so designed that, when rotated at a high speed, it causes a stream of fine bubbles of the gas to circulate through the liquid, thus ensuring equilibrium between the liquid and the gas.

The manometer is provided with a scale of millimetres etched on the glass.

IV. Calibration of the Apparatus.

In order to check the formula derived for the calculation of the volume of gas absorbed, use was made of ferrous hydrate as an absorbent for oxygen. The following experiments were made :—

The apparatus was filled with 110 c.c. of distilled water which had been previously saturated with air at 20° C. by bubbling air through it for some hours, and the water circulation from the thermostat through the water-jacket started. When everything was in equilibrium, about 25 c.c. of the water was withdrawn, and in place of it was added exactly 10 c.c. of a solution of ferrous sulphate containing 8·2 grams per litre, followed by 10 c.c. of a 10 per cent. solution of sodium carbonate, the whole being carefully washed into the apparatus. The barometer was then read, and the taps of the apparatus having been suitably adjusted, the stirrer was started, and the manometer watched until the reading became constant. The maximum reading was then used to calculate the volume of oxygen absorbed by the ferrous hydrate.

Experiment A. — Temperature, 20·0° C ; barometer, 768·1 mm.

Maximum reading of manometer	114·0 divisions.
Second reading after resetting to zero.	5·5 „
114 divisions at 768·1 mm. correspond to	1·525 cm.
5·5 „ „ „	·073 „
Total ...	1·598

Total volume absorbed, calculated for N.T.P.= 1·504 c.c.

Experiment B.—Temperature, 20° C.; barometer, 769·9 mm.

Maximum reading of manometer, 118 divisions.

118 divisions at 769·9 mm. correspond to 1·610 c.c., which at N.T.P. reduces to 1·520 c.c.

The mean of the two experiments gives 1·512 c.c. absorbed.

Since the partial pressure of the oxygen in the air in the vessel was reduced from $\frac{10·5}{50}$ to $\frac{9·0}{50}$, a correction for this must be applied. The pressure in the vessel before the experiments was 768·1 mm., and at the end was 758·0 mm.

Taking the composition of atmospheric air to be approximately : nitrogen, 79 per cent., oxygen, 21 per cent., and the coefficient of absorption of oxygen as 0·0310 at 20° C., we can calculate the amounts of oxygen in solution at the beginning and at the end of the experiments.

The pressure of aqueous vapour at 20·0° C. is 17·5 mm. The volume of oxygen in solution at the start is :

$$V_0 = \cdot 0310 \times 110 \times \frac{10 \cdot 5}{50} \times \frac{750 \cdot 6}{760} = \cdot 706 \text{ c.c.}$$

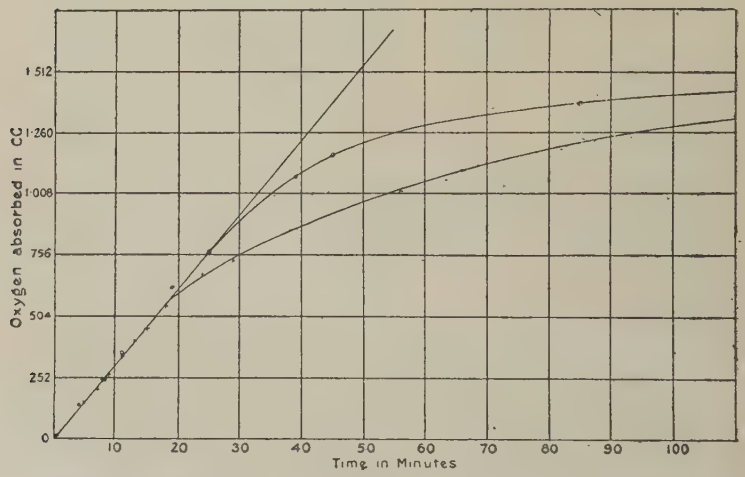
The volume in solution at the end is :

$$V_1 = \cdot 0310 \times 110 \times \frac{9}{50} \times \frac{740 \cdot 5}{760} = \cdot 598 \text{ c.c.}$$

Hence the difference due to change in the saturation value is ·108 c.c., and this, when added to the volume indicated by the manometer reading, gives a total of 1·62 c.c. as the actual absorption.

The 10 c.c. of ferrous sulphate used should have absorbed 1·64 c.c. oxygen according to its titre by potassium permanganate, hence the two values agree within $1\frac{1}{4}$ per cent.

Fig. 3.



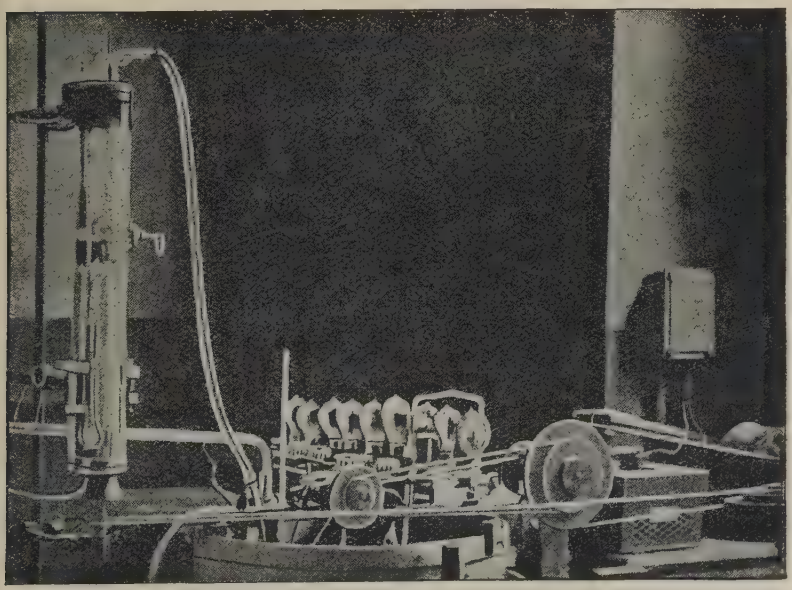
The graph, fig. 3, shows the course of the absorption. During the first part of the absorption the water is completely de-aerated by the excess of ferrous hydrate, and, consequently, the oxygen is absorbed at a constant rate, as shown by the fact that the graph at this portion is practically a straight line. In the second stage, when all the ferrous hydrate has been oxidized, the absorption falls off gradually, so that the graph becomes a logarithmic curve. During this stage the water becomes completely re-aerated. In the figure, the second graph shows a more gradual approach to saturation than the first; this is due to the fact that during this

experiment the speed of the motor driving the stirrer varied suddenly owing to variation in the voltage of the supply. This observation indicated the advisability of determining the time necessary to attain equilibrium under certain conditions. As this was intimately connected with some work which had been done previously on the rate of solution of gases by water, it was considered worth while to examine it more fully.

V. Experiments on the Effect of Stirring on the Rate of Solution of Oxygen in Water.

The method consisted in introducing into the apparatus known amounts of a solution of ferrous sulphate and precipitating the hydrate by means of a solution of caustic

Fig. 4.



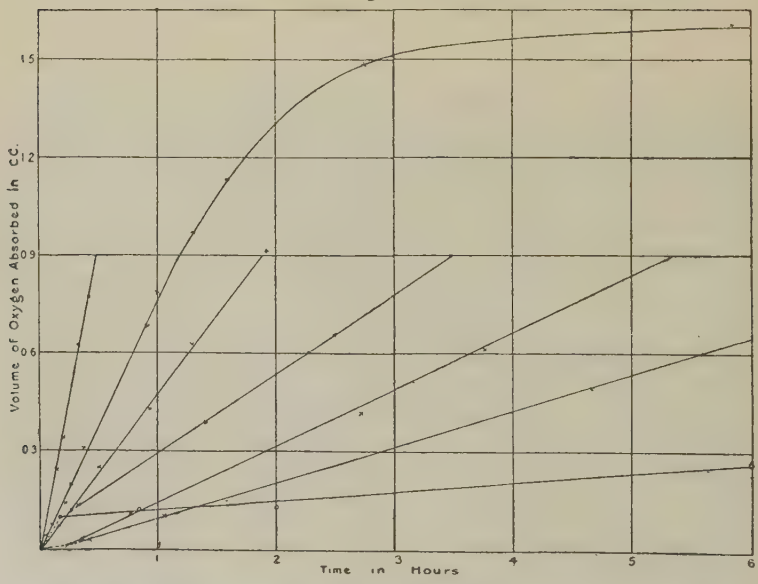
potash ; the stirrer was then driven at certain definite speeds by means of a small alternating-current motor (which could be relied upon not to vary in speed to any large extent), and the rate at which the oxygen was absorbed noted by observing the manometer.

The complete apparatus used for these experiments is shown in the photograph (fig. 4). The motor at the right of the picture drives the small circulating pump (which is

immersed in the water in the thermostat), and also a stirrer in the thermostat. The water is pumped along the horizontal glass tube to the left, and into the water-jacket of the apparatus already described, from which it returns to the thermostat by the rubber tube from the top.

To the extreme right will be seen one of a series of horizontal pulleys which we connected to the small alternating-current motor in order to give the desired variation in speed of stirring. This pulley is connected to the stirrer of the apparatus by the long belt appearing in the foreground, thus imparting motion to the stirrer at a rate which could be determined by the ratio of the various pulleys. The water

Fig. 5.

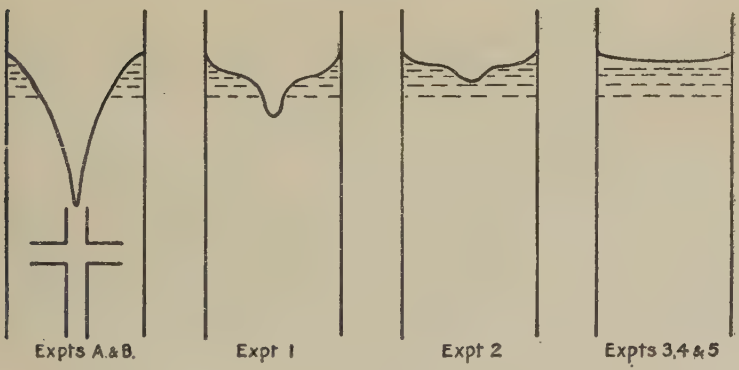


circulation was continued, and the stirrer run at a constant speed during the course of each experiment. The lower speeds of revolution were counted directly, using a stop-watch to check the time, and for the higher speeds the rate of one of the slower-moving pulleys was found and that of the stirrer by calculation.

Five experiments were made with different rates of stirring, and one experiment was made to compare the rate at which quiescent water absorbs oxygen with the rates at which the thoroughly stirred water absorbs it. The results of these experiments are shown in fig. 5.

The rate of stirring in these experiments varied from zero to about 1000 revolutions per minute. The lower rates up to about 140 revolutions per minute did not appreciably distort the surface of the water, but above this speed the surface varied in shape and area with each variation in the speed of the stirrer. The shapes assumed by the water surface are shown in fig. 6; and it will be seen that they range from the nearly flat surface of still water to the point at which the air is drawn down into the water in small bubbles. At this point the surface area becomes uncertain, so that no conclusions can be drawn from experiments at higher speeds. In the other cases the surface area was taken to be approximately equal to that of a cone with the

Fig. 6.



vertical axis equal in depth to that attained by the lowest point of the water surface.

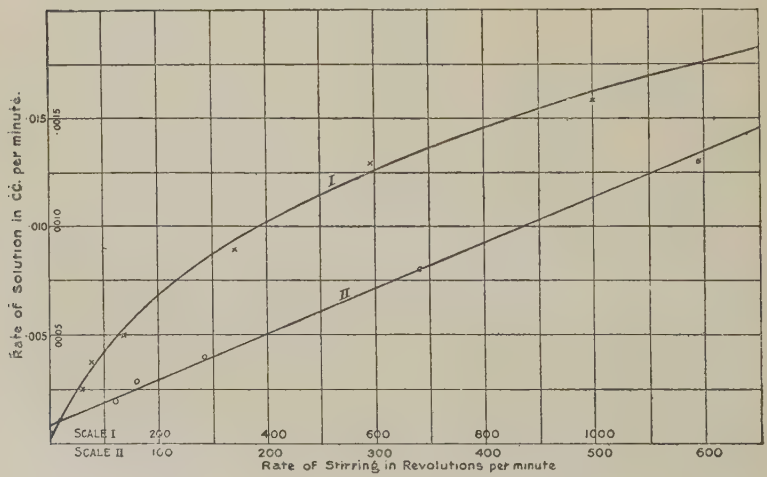
The progress of the absorption followed a linear law, as will be seen from the graph, fig. 5, and this shows that the ferrous hydrate de-oxygenated the water completely almost at once, so that the rate of solution of the oxygen remained constant until all the hydrate was oxidized.

The variation in the value of the rate of solution with stirring is shown in the table and in fig. 7. On the graph the lower line shows the rate of solution under the conditions of the experiment plotted against rate of stirring, and the points lie approximately on a straight line. Hence under the conditions of these experiments the rate of solution varies directly as the rate of stirring.

Values of Rate of Solution for different Rates of Stirring.

Experiment.	Speed of stirrer, r.p.m.	Estimated areas of surface, sq. cm.	Rate of solution in c.c. per min.	Rate of solution per unit area. $S=\frac{a}{A}$.
A and B.	1000	19·0	·030	·0016
1	590	11·1	·014	·0013
2	340	8·8	·008	·0009
3	140	8·1	·004	·0005
4	80	8·1	·003	·0004
5	60	8·1	·002	·00025
6	0	8·1	·0001	·00001

Fig. 7.

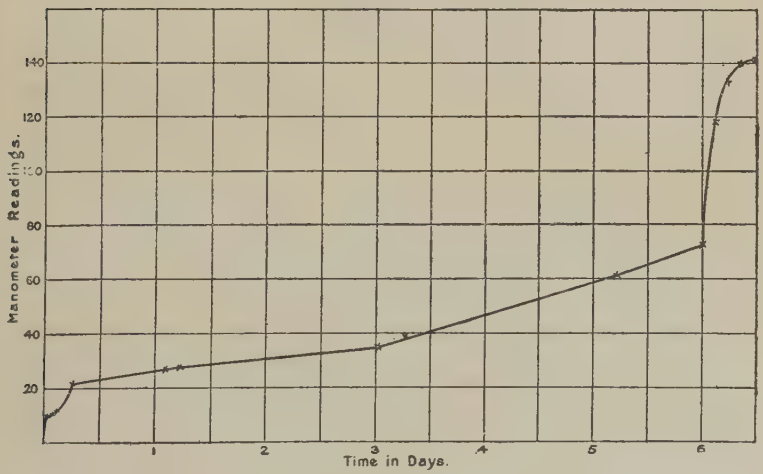


When, however, the effect of increased surface area is taken into account, and the rate of solution per unit area plotted against rate of stirring, the result is the upper line in fig. 7. This curve shows the rapid increase in the rate of solution at first, which gradually falls off as the higher values are reached, and tends to reach a maximum.

VI. Comparison of Results.

The results obtained in Experiment 6 are shown as a graph in fig. 8 in order to afford a comparison between the rate at which the oxygen is absorbed by quiescent water and the rate when the water is stirred. The water was at first stirred for two minutes in order to mix the ferrous hydrate with the liquid, and thus reduce the oxygen content to zero. During this period the rate of absorption was of the same order as obtained in the other experiments. The stirring was then stopped, and the rate fell off slowly as the liquid

Fig. 8.



came to rest until it reached a value which remained nearly constant for three days. On the third day this suddenly changed to a higher value, which remained constant until the sixth day, by which time only about half the saturation value had been reached. The liquid was then stirred again, and the remainder of the absorption was completed in about five hours. Hence a process of absorption which may take many days to complete when the water is quiescent takes place in as many hours with moderate stirring.

The sudden change in the rate of solution of oxygen by the quiescent water indicated above is characteristic of the process under these conditions, for the rate of solution of gases by water is then liable to sudden and unaccountable variations within narrow limits.

The greatest value for the rate of solution per unit area

given in the table represents the maximum rate attainable under the conditions of these experiments, without allowing the surface exposed to become indefinite: hence it is of interest to compare this with the rate of solution as determined in previous experiments *.

The rate of solution of oxygen into air-free water has been found by a totally different method to be ·0161 c.c. per minute per square centimetre of area exposed. Hence for the oxygen in the atmosphere the rate should be $\cdot 0161 \times \frac{21}{100} = \cdot 0034$ c.c. per minute under similar conditions, since the rate of solution has been shown to be proportional to the partial pressure.

This value is more than twice as great as the maximum value attained in these experiments (·0016), showing that the rate of mixing that was reached under these circumstances was not so rapid as that obtaining in the experiments referred to. This was to be expected, since in those experiments the water was exposed to the oxygen in very thin layers, and very perfectly mixed immediately afterwards. However, the fact that the two values come so near each other shows that with more perfect stirring arrangements it might be possible to approximate very closely to the maximum rate of solution.

These experiments therefore afford a connecting-link between the conditions obtaining in the work referred to and those obtaining in nature. They also emphasize the important part played by mixing of the water in determining the rate of solution. It will be seen on reference to the table that very gentle stirring of the under layers of the water increases the rate of solution as much as twenty-fold as compared with the stationary water. This bears out the view put forward previously †, that the rate of solution of air by water under ordinary conditions is largely determined by the rate of mixing. Experiments are being continued with this apparatus; and it is hoped to publish further results in the future.

Chemical Department,
Royal College of Science, Dublin.

* Adeney and Becker, Scientific Proc. R. D. S. xv. p. 625 (1919).
† Adeney and Becker, Scientific Proc. R. D. S. xvi. p. 143 (1920).

LX. *Some Photoelectric Experiments on Platinum relating to the Influence of Gases.* *By* Lars A. Welo, *Ph.D.**

AMONG the problems in connexion with the photo-electric effect it seems that none has led, for so long a time, to such conflicting experimental results and hence to so wide a difference of opinion as that concerning the influence of gases. Among those who dissent from the prevailing view that gases are merely of secondary influence are to be mentioned, particularly, Hallwachs and his students †. The reason for the differing results and opinions is, I believe, that attention has been directed too much towards the entire elimination of gases without a study of the change in photo-sensitiveness when the gas is being removed. The complete removal of gas is extremely difficult and is always a questionable achievement. A more certain procedure would seem to be to observe the changes of photo-sensitiveness accompanying a gradual removal of gas and then, by a sort of process of passing to the limit, on the basis of the observed changes, draw conclusions as to the effect to be expected when all the gas is removed.

This plan has been adopted by M. Sende and H. Simon ‡ at the suggestion of Hallwachs. By heating a platinum foil in a vacuum at fixed high temperatures, they have obtained the sensitiveness as a function of the time of heating. Discontinuing the experiment at too early a stage and consequently approaching the limit on the basis of incomplete data, they have come to conclusions that must be said to be quite erroneous.

Another procedure on this principle is that first used by Piersol § and later by myself ‖. The metal foil is heated at various increasing heating currents and the photo-sensitiveness is determined after the foil has become cool. The curve showing the sensitiveness as a function of the heating current with which gas was driven off, exhibits marked maxima and minima. The experiments herein described are of this type and may be regarded as in continuation of those previously reported upon, under improved experimental conditions.

* Communicated by Professor Gustaf Granqvist.

† See, among other papers: G. Wiedemann and W. Hallwachs, *Verh. d. D. Phys. Ges.* xvi. p. 107 (1914); W. Hallwachs, *Phys. Zeit.* xxi. p. 561 (1920); H. Küstner, *Phys. Zeit.* xv. p. 68 (1914); M. Sende and H. Simon, *Ann. d. Phys.* lxv. p. 697 (1921).

‡ *Ann. d. Phys.* lxv. p. 697 (1921).

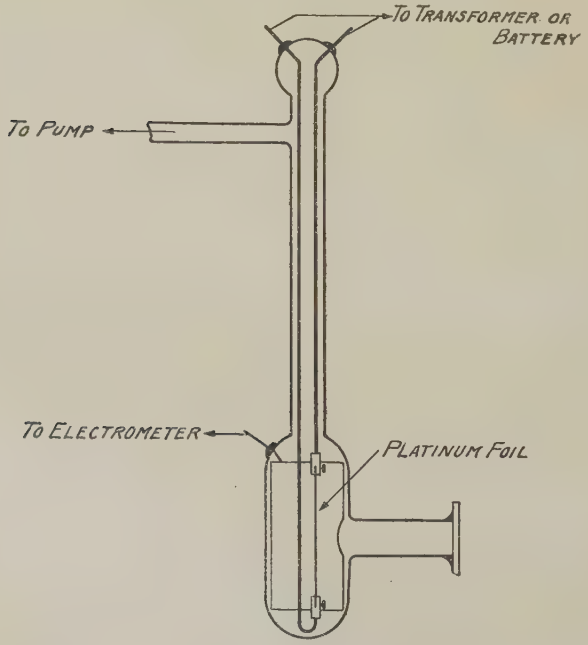
§ Phys. Rev. viii. p. 238 (1916).

‖ Phys. Rev. xii. p. 251 (1918).

The original aim was two-fold. First, to work in much higher vacua in order to eliminate possible effects of residual gases. Second, to use two extreme wave-lengths for which platinum is sensitive, rather than the total radiation ; making possible, not only conclusions as to the manner in which gas affects the photoelectric effect, but also as to the structure of the adsorbed layer. As the work proceeded, it became apparent that time is quite as important a factor in the removal of occluded and adsorbed gases as high temperatures and high vacua. Accordingly, heating-current–photo-current curves were obtained after the platinum had been heated in a vacuum for a very long time. On the basis of the changed type of curve thus obtained, the principal conclusion is drawn : namely, that the platinum itself is the seat of electronic emission and that the layer of gas at the surface merely hinders their escape.

The Apparatus and Method of Experiment.

Fig. 1.



In the early part of the work when emphasis was placed on very high vacua and the fullest possible elimination of vapours, the tube shown in fig. 1 was used. All glass joints

were blown, as was also the direct connexion to the Volmer condensation pump. A hard white sealing-wax was used to attach the quartz plate. Eight sealed-in platinum leads entered the tube at the top and were welded in groups of four to the iron wires supporting the platinum foil. The receiving electrode was an oxidized copper cylinder completely surrounding the foil, except for a small opening to admit the radiation. The platinum foil was 6 cm. long, 3·4 mm. wide, and 0·08 mm. thick.

Fig. 2.

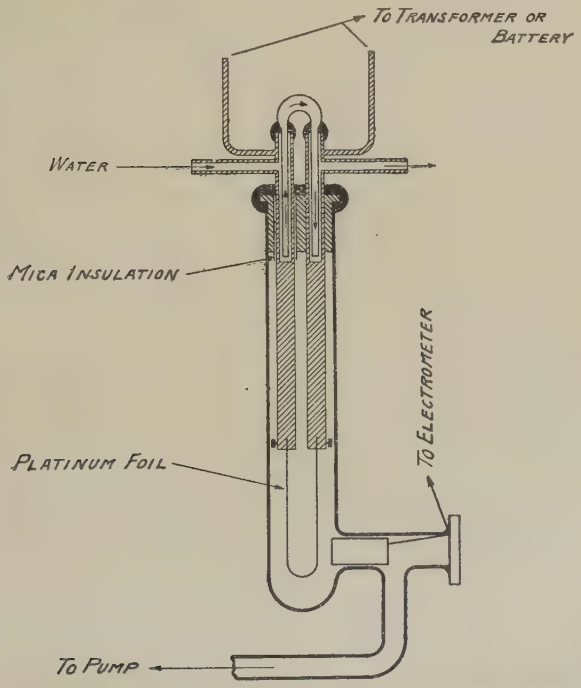


Fig 2. shows the tube used later, when it was known that residual gases and vapours at low pressures play a negligible part, and when some cooling arrangement was necessary while heating for a long time. It was designed to make use of longer foils in order to reduce the effects of gas diffusion from the cold ends. The foils were of the same width and thickness as before, but 13 cm. long and mounted in the form of a U. The receiving electrode was a copper cylinder slipped into the side tube admitting the radiation. The brass rods passed through a brass stopper closely fitting the

glass tube. One of the rods was insulated with mica. Picein was used to make the joints tight and also to attach the quartz plate.

The Volmer condensation pump was backed by a Gaede mercury and oil pump. A McLeod gauge between the pumps showed that the back pressure on the condensation pump was easily kept less than 6×10^{-5} mm. of mercury when the foil was not being heated. From observations with the induction-coil discharge it is known that the pressures in the tubes were much smaller. During a run the condensation pump was continually operated. The other pumps were only run from time to time to keep the back pressure small. When the foil was to be heated, connexion was made to a step-down transformer. When the photo-electric current was to be measured, the transformer connexion was broken and connexion made with the negative pole of a 125 volt battery so that saturation was certain. The currents were measured by the high resistance method. The resistance of about $4{\cdot}5 \times 10^{9}$ ohms was a fine, long capillary tube containing a 10 per cent. solution of alcohol in xylol. The electrometer had a sensibility of 520 mm. per volt at 1·5 metres distance. A Heraus quartz mercury lamp served as source of radiation. Its constant power consumption was frequently checked during a run. The slit-width of 1·5 mm. was rather large, so that the light, after passing through the Hilger monochromator, was not strictly monochromatic. In view of the decided differences obtained with the extreme wave-lengths employed it was not deemed necessary to have the light purely monochromatic. Ten minutes was adopted as the standard time of heating with each current, although times of 5 or 7 minutes gave the same type of curve. The photoelectric currents were generally measured two minutes after heating was stopped. In the latter stages of the work when the foils were more nearly gas-free, the photo-sensitiveness was rather unsteady, and it was necessary to wait until a fairly constant value was reached.

Independence of Degree of Evacuation.

As remarked in the foregoing, a heating-current–photo-current curve shows marked maxima and minima. The process of getting rid of gas seems to be accompanied by some complicating features. One would expect that the photo-sensitiveness should gradually increase or that it should remain constant beyond a certain heating-current.

In my former paper * I discussed a possible explanation if one supposes that active layers are built up from residual gases and vapours whose effect is superposed upon that of the metal ; or, that a destructive layer from the same source is the cause of the depressions in the curve. The curves of fig. 3 † afford a test on this point when compared with the previously published curves of Piersol and myself. The vacua of the present experiments were of the order 10^{-6} mm. of mercury and at least 100 times better than before. The variations beyond the first maximum should thus be much less marked if not entirely absent. In fact, they are still enormous and fully as pronounced as in the former work. The source of the disturbing gas-layer is, then, the occluded or dissolved gas in the platinum itself, and not that which remains in the tube. This result was confirmed later in that the irregularities in the curves disappeared after heating and pumping for several hours.

In fig. 3 the curves to the left are for the original run on a piece of platinum subjected to no treatment, aside from washing in acid and distilled water, followed by thorough drying. The curves to the right are for the same foil after it had stood, for 40 hours, in dry air admitted immediately after completing the original run. It will be shown in a following section of this paper that air has little or nothing to do with the shapes of these curves. Except in their first part, similar curves would have been secured if the second run had been made immediately on completing the first. It will be noted that the first maximum in the left-hand curve is not fully developed. The peak was missed since no observation was made at 2 amperes of heating-current.

Differences with respect to Wave-lengths.

The possibilities in the way of explaining the varying sensitiveness observed in a heating-current–photo-current curve may be summarized as follows :—

(1) Change of Photoelectric property of Metal.
  (*a*) Chemical combination with gas.
  (*b*) Change of gas concentration.

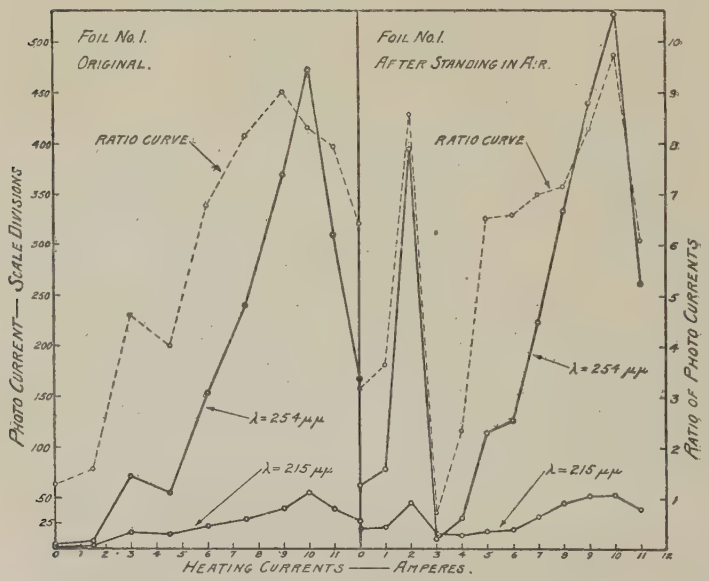
(2) Absorption of a Constant Initial Emission.
  (*a*) Transition Layer theory of Adsorption.
  (*b*) Layer one molecule thick.

* *Loc. cit.*

† The smaller heating-currents shown here are due to the use of narrower foils.

The first possibility is readily tested by observations on the long wave limit at various heating-currents. No shift of the wave-length limit was observed, either during the runs shown in fig. 3, or in any of the later runs made on other foils. Special effort was made to detect such changes at the peaks of the curves or at heating-currents corresponding to low sensitiveness. Similar results with respect to constant wave-length limits have been reported by Koppius*, although the absolute value of the photo-current from pure platinum

Fig. 3.



varied somewhat with the temperature and very much with time. Possibility (1) is thus excluded and with it the need of deciding between (*a*) and (*b*). This statement is, of course, subject to the validity of the general rule that the photoelectric wave-length limit is a characteristic constant for an element or a compound.

If, during an experiment of this sort, we make observations with two extreme wave-lengths instead of the total radiation, it is possible to decide between the cases (*a*) and (*b*) of the remaining possibility. In the transition layer theory of

* Phys. Rev. xviii. p. 443 (1921).

adsorption the gas is assumed to constitute a miniature atmosphere at the surface. Cleaning of the substance is looked upon as a decrease in the thickness or density of the adsorbed layer. In the primary valence theory the layer is imagined to be, on the whole, only one molecule thick, and cleaning must be thought of as the opening up of gaps or clean patches on the surface.

The differences with respect to the effect on the electron emission is apparent. In the case of the transition layer there will be selective absorption with regard to the electron's velocity. The relative proportion of slow and fast electrons breaking through the layer and reaching the receiving electrode will depend on the stage of cleaning. On the other hand, if cleaned patches are formed on the surface, all of the emitted electrons, fast or slow, reach the receiving electrode, while all of the electrons emitted from the gas-covered metal are stopped. If one is to assume a layer of molecular thickness at all one must also make this last assumption in order to account for the low sensitiveness before cleaning, even with short wave-length radiation.

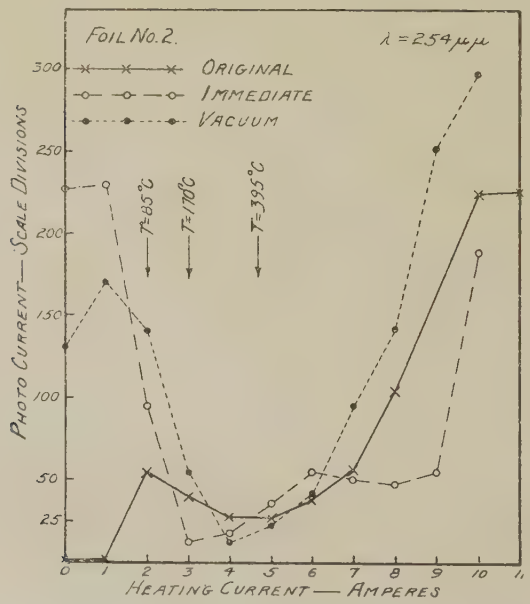
The ratio of the photo-current for the long-wave radiation to the photo-current for radiation of short wave-length thus becomes the test between the two theories of adsorption. The relative intensities of the two radiations must, of course, be constant. Since the slower electrons are absorbed, the peaks and the depressions in the curves should be more prominent in those for radiation of long wave-length. The ratio, at each heating-current, of the two photo-currents will not be constant but will be larger when the sensitiveness is high. If, on heating, clean patches are formed, the photo-emission for each wave-length is proportional to the total clean area and the ratio should be the same at all heating-currents.

The results of this test are shown in fig. 3. The conditions under which the data were taken are described in the preceding sections. The observations with the two radiations were, of course, made during the same runs and for each heating-current, at as nearly the same time as possible. The scale of ratios is at the right. They are seen to vary from less than one to almost 10, so that the test is decisively against the primary valence theory of adsorption. There must be an atmosphere of more than molecular thickness, or some equivalent system, which sifts out the slowly moving electrons.

Repeated runs on the same Foil.

Fig. 4 shows the original and two typical repetition curves for a new foil. "Immediate" means that the run was made immediately after completing the previous run. "Vacuum" means that the foil had stood in the exhausted tube for some time following the previous run or heating, in this case 91 hours. The lower absolute values of the photo-currents, as compared with fig. 3, are due partly to the use of another foil and partly to the fact that another tube (see fig. 2) was employed. In this tube the receiving

Fig. 4.



electrode is placed in front of the foil and does not completely surround it so that some of the electrons may miss the electrode. The original and immediate curves are consecutive, while the vacuum curve is for the fifth run. Similar immediate and vacuum curves were obtained even after a dozen runs had been made, showing that the disturbing gas is not removed during one or even several runs. In each succeeding run, however, the minimum at 4 amperes of heating-current becomes less and less marked. Time is required as well as high vacua and temperatures in order to remove the gases.

The Temperatures.

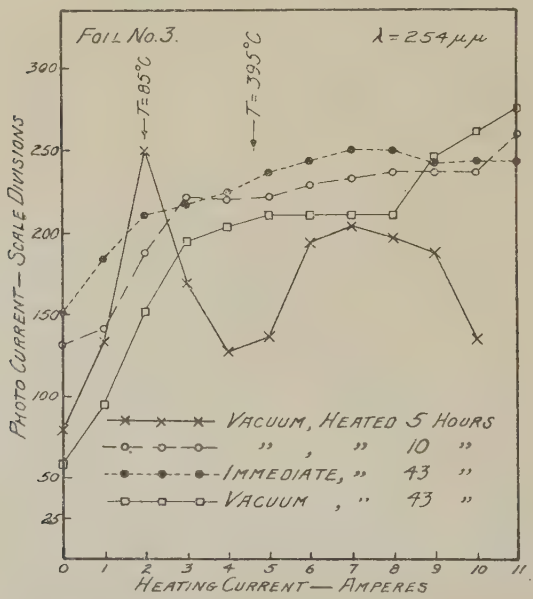
In fig. 4 and the succeeding figures the approximate temperatures corresponding to the most interesting parts of the curves are given. They are taken from a calibration curve determined by fusing small bits of substances of known melting-points on the foils when the work was completed. The heating-current necessary to raise the foil to the melting temperature was noted. The substances were: paraffine, 42°·5 C.; sulphur, 112°·5 C. and potassium bichromate, 395° C. The heating-currents at melting were, respectively, 1·13, 2·42, and 4·63 amperes. The temperature corresponding to a heating-current of 11 amperes is estimated to be about 1300° C. The maximum heating current was as high as possible consistent with a barely perceptible evaporation of the platinum.

Continued Heating at High Temperatures.

In fig. 5 we see the importance of time as a factor in the removal of occluded or dissolved gases. Foil No. 3 was cut from the same sheet and adjoining foil No. 2. Since the same tube (fig. 2) was employed, the absolute values of the photo-currents are comparable with those shown in fig. 4. The heating was done at 11 amperes. It was not continuous, and the times indicated merely show the total time of heating. A vacuum curve taken after 5 hours of heating shows the usual minimum, but it is not so well developed. When the total time of heating is extended to 10 hours the minimum in a curve has disappeared. Now, for the first time, a curve of the expected form is realized: namely, one showing an increase in photo-sensitiveness at first and an approach to constancy at the larger heating-currents. It was expected that by heating for a still longer time, the vacuum and especially the immediate curve should show greater constancy of photo-sensitiveness during a run. The vacuum curve after heating 43 hours is not essentially different from that secured after 10 hours of heating. Contrary to expectation, the immediate curve shows that the foil is not at its highest sensitiveness immediately after a long period of heating. The gradual rise is not accidental, for it was observed during other similar runs. In the vacuum curves the gradual rise is due to the removal of the fatigue effect introduced by the residual air which is present in the tube in very small amounts. In a following section it will be seen that so large a fatigue does not occur in the presence of other gases.

The curves of fig. 5 represent, it is believed, the closest possible approach to the "ideal" heating-current–photo-current curve. It is not claimed that the gases are entirely absent, but the remaining quantities are so small after 10 or more hours of heating that not enough remains to develop the minima so prominent in the original and in the repetition curves. Further, the fundamental photoelectric current for platinum is seen to be that of the maxima in the earlier

Fig. 5.



curves. There is seen to be, always, in these curves of fig. 5, an approach to the limiting sensitiveness of about 250 scale divisions under the existing experimental conditions. The limiting value is never zero.

The Gases Emitted.

The gases driven from the foil were frequently examined with a spectroscope during the 43 hour period of heating. The condensation pump forced them into a large bulb in connexion with a Geissler discharge-tube of small volume. With mercury, the gases in the bulb were compressed into the discharge-tube to suitable pressures. During the first 12 hours of heating the only lines or bands to be seen were those of carbon dioxide. According to Kayser * the same spectrum is given by carbon monoxide. After 12 hours of

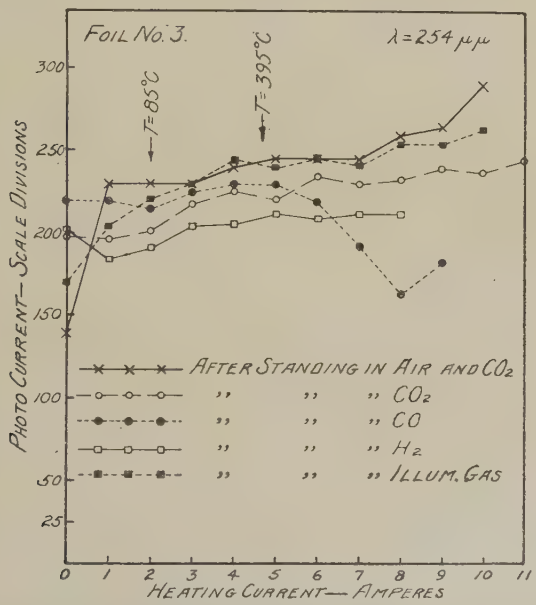
* *Handbuch der Spektroskopie.*

heating the carbon compounds disappeared and the hydrogen lines alone were seen. A marked diminution of the rate of gas emission also occurred when their character changed.

Gas Treatment not Effective.

The attempt was made to reintroduce the irregularities in the curves by letting the gas-free foil stand in gas from 1 to 4 days. In view of the spectroscopic results it was natural to try the oxides of carbon and hydrogen and finally air. As these gases failed to introduce the irregularities, particularly the minimum at 4 amperes of heating-current, an

Fig. 6.



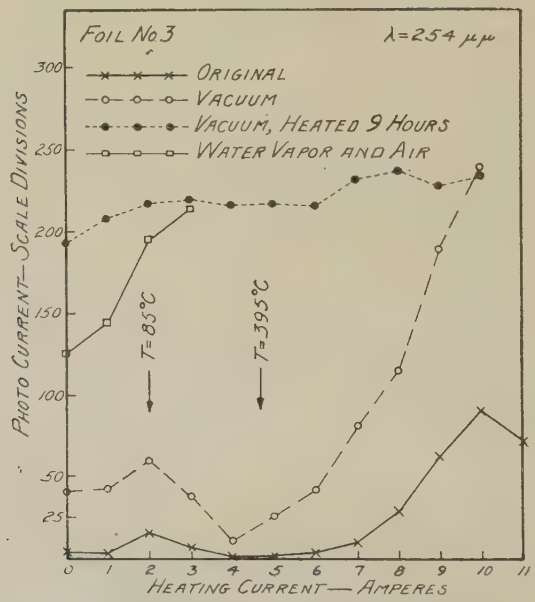
attempt was made with city illuminating gas. The possibility as to variety is great with this gas. It also failed. The resulting curves shown in fig. 6 are of the same general type as those of fig. 5, and the approximate absolute value of the limiting photoelectric current is again 250 scale-divisions. The differences in the cases of hydrogen and carbon monoxide are probably accidental since these gases are present in illuminating gas. At any rate the looked for minimum was not found. It is noted that for air and the illuminating gas, which contains traces of air, the initial photo-sensitiveness is lower than for the other gases. This indicates that the fatigue discussed in connexion with fig. 5 is to be traced to air.

These generally negative results are in direct conflict with some of those I reported in a previous paper *. It is quite evident now that the effects I once attributed to added gases are due to the remaining gases in the foil. The need of long periods of heating was not realized at the time.

Effect of Heating in Flame.

The original behaviour with respect to gases can, however, be introduced by heating in a flame. The blow-torch was allowed to play, on the part of the foil subjected to radiation, for about 15 minutes. The platinum became white hot.

Fig. 7.



After remounting and evacuating, the original curve of fig. 7 was secured. It is of the usual type, but the photo-currents are for some unknown reason smaller. The vacuum run made 20 hours later is not only of the expected type but the usual sensitiveness of 250 scale-divisions is approached at the end. The second vacuum run was made after heating with 11 amperes for 9 hours. The foil is again nearly gas-free, and the curve is like those of fig. 5 both as to type and the values of the photo-currents. The gases which disturb the photoelectric emission of platinum are shown to be introduced during the process of its preparation.

* *Loc. cit.*

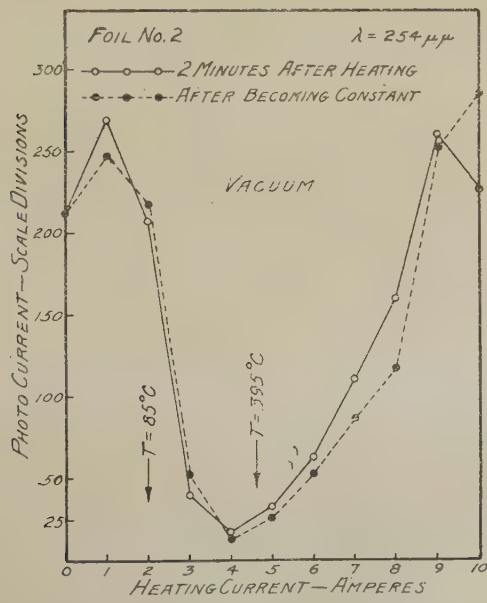
The results of this section exclude the bare possibility that the greater regularity in photo-sensitiveness shown in figs. 5 and 6 is caused by a more stable crystalline structure given to the platinum when it is heated for a long time.

The influence of water vapour has been much discussed in the literature of the photoelectric effect. The experiment was tried of letting the foil stand over-night in water vapour. A little air accidentally entered. The short curve of fig. 7 was obtained. It was not continued since its course is exactly as if the foil had stood in a vacuum or in the presence of air only.

A Small Time Effect.

It has been mentioned that when the metal becomes nearly gas-free, the photo-currents are rather unsteady after each heating. During the original run, however, and the first few repetition runs the time variation is small and has a perfectly definite direction depending on the heating-current. It was

Fig. 8.



observed that while working on the ascending part of the heating-current–photo-current curve the sensitiveness decreased after heating, but that on the descending part the sensitiveness increased. Fig. 8 gives the results of a more

detailed study of this phenomenon. It represents an early vacuum run, so that the foil still contains much gas. The curve drawn solid is based on readings taken 2 minutes after heating. The broken curve is for readings taken after constancy is reached following each heating. The changes are proportionally small and do not affect the type of curve.

Such a vacuum run was once discontinued at the minimum at 4 amperes, and the foil allowed to remain in the vacuum until the next day. The run was again taken up, beginning with 5 amperes of heating-current. The curve duplicated those of fig. 8. Interruption of the run does not affect the type of curve. The type of curve is determined by the stage of gas elimination only and is not modified by superposed time effects.

Primary Photoelectric Effect independent of Gas Content.

Let us first consider the most likely explanation of the minima of the heating-current–photo-current curves. It has already been concluded that they are due to the absorption of the slowly moving electrons by the miniature atmosphere covering the platinum. The formation of this atmosphere at particular temperatures or heating-currents and its entire absence at others is readily conceived. The elimination of gas from a metal involves two distinct processes. In one the gas must be carried to the surface by diffusion. In the other the gas must be released from the surface. Diffusion is known to increase continually with the temperature. The release of gas is generally considered to be in the nature of a threshold phenomenon and does not become marked until particular temperatures characteristic of the system solid–gas are attained. Equilibrium between the two processes is brought about by an adjustment in the thickness or density of the layer of gas. The thickness or density thus becomes a function of the temperature, or, more specifically here, the heating-current. Take, for example, the minimum in the heating-current–photo-current curve at 4 amperes where the temperature is 290° C. On the present view the equilibrium requirement is a dense or thick layer. At succeeding heating-currents the release of gas is more rapid in proportion to the diffusion, and equilibrium is established with a thinner or less dense layer. To account for the development of a minimum beyond 10 amperes of heating-current, it is only necessary to assume the existence of another gas having a smaller temperature coefficient of

diffusion and a higher threshold temperature of release. The assumption that another disturbing gas is present is believed to be justified since the second minimum seldom appears in other than the original runs. When released it evidently comes very rapidly. Then, too, it may be present in only small amounts.

The view that has been outlined gains support from the time effects described in the preceding section. After a heating on the descending part of the curve, the accumulation of gas is greater than the equilibrium requirement as the metal cools. The gas diffuses back into the metal and the photo-current increases. On the ascending part, more gas is required for equilibrium on cooling, and it can come from the metal by diffusion or from the tube until the pumps have had time to reduce the pressure.

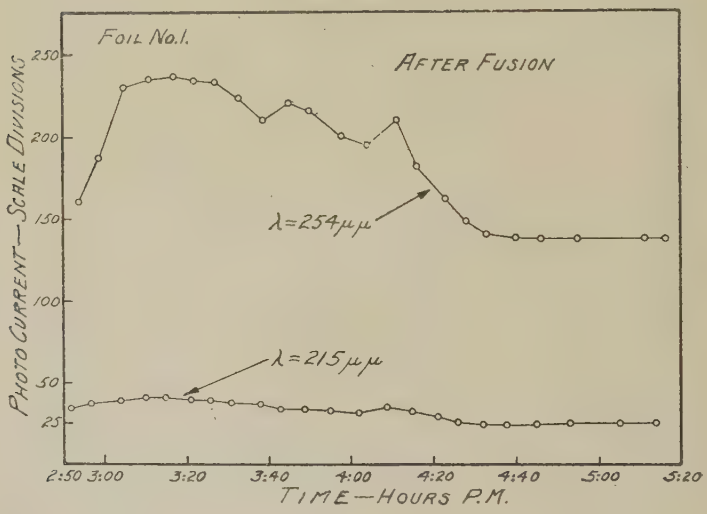
The results recently published by M. Sende and H. Simon* receive an entirely different interpretation if the foregoing view is adopted. We will direct our attention first to fig. 9 of their paper, according to which the photo-sensitiveness of platinum was reduced to $\frac{1}{60}$ of its maximum value by repeated heating at a fixed high temperature. They consider that the gas is nearly gone and that by further heating a limiting photo-sensitiveness of zero would be approached. It is most probable that their experiment was discontinued just at the stage when an absorbing layer of gas was at its greatest thickness or density in order to maintain the equilibrium between the rate of diffusion and the rate of release from the surface. A mere beginning had been made in the way of removing gases since the total time of heating was only 130×20 seconds or 43 minutes. Times of the order 9 hours were necessary in the writer's experiments. The writer believes that he could, with equal justification, extrapolate the original curves of fig. 3 of the present paper (especially for $\lambda = 254\,\mu\mu$) beyond 12 amperes of heating-current and claim that the photo-electric effect of platinum vanishes when the gas is gone.

The same experimenters observed the sensitiveness of platinum immediately after fusion in a very high vacuum. It was less than $\frac{1}{1000}$ of a previous maximum value. Fig. 9 of this paper represents the writer's results in a similar experiment. The accompanying time changes are shown. The platinum was fused, after completing the runs shown in fig. 3, in a vacuum of the order 10^{-6} mm. of mercury. Although the photo-currents are smaller than the maxima shown in fig. 3

* *Loc. cit.*

they are by no means zero. At most three minutes elapsed between the time of fusion and the first measurement, so that it is not possible to extrapolate backward to zero photosensitiveness. Nor can it be said that the electrons come from the supporting iron wire behind the foil. The portion of platinum that was fused was less than a tenth of that illuminated. Moreover, the final values of the photoelectric current are smaller than the initial.

Fig. 9.



The smaller sensitiveness shown here and the close approach to zero sensitiveness in the experiment of M. Sende and H. Simon is readily explained on the theory of an absorbing layer. During fusion the increase of temperature is very sudden. If much gas remains the contribution to the surface by diffusion overwhelms the rate of release. The time of fusion is, however, too short to allow of the equilibrium adjustment to a thinner or less dense layer.

Conclusions and Summary.

The photoelectric effect in platinum has been studied as it is changed by increasing temperatures of heating in a high vacuum. The effect, measured after cooling of the metal, was plotted against the heating-current. The wave-length

limit proved to be constant, but the largest variations in sensitiveness took place with radiation of long wave-length. It is concluded that the primary emission from the platinum is constant but that an adsorbed layer of gas, whose effectiveness depends on the temperature of heating, stops the electrons of low velocity.

The evidence is considered to be in favour of the transition layer theory of adsorption and decisively against the view that the adsorbed gas consists of a single layer of molecules.

The type of curve becomes very different after the foil has been heated at as high a temperature as possible for a time of 9 hours or more. The minima of the original curves do not appear. There is always an approach to a sensitiveness of approximately 250 scale-divisions under the given experimental conditions. The sensitiveness never approaches zero. Hence the photoelectric property is primarily that of the platinum itself. The gases merely modify and always reduce the effect.

The minima of the original or repetition curves could not be reintroduced by letting the gas-free foil stand in various gases. They were reintroduced by heating with a blow-torch.

The minima of the curves are qualitatively explained in a simple manner by considering the driving off of gas as involving two distinct processes. In the first, the gas is brought to the surface by diffusion and in the second it must be released. At each heating-current or temperature, with given gas concentration in the metal, a gas layer of characteristic thickness or density brings about the equilibrium adjustment.

The experiments were performed at the Physical Institute in Uppsala. I wish to thank the Staff of the Institute and particularly its Director, Professor Gustaf Granqvist, for the aid and equipment placed at my disposal and the many courtesies shown me during my year of study in Sweden.

Physical Institute,
Uppsala, Sweden.
April 25, 1922.

LXI. *On the Theory of Generalized Quanta and the Balmer Lines.* *By* S. C. Kar*.

THE general principles governing the quantaic structure of phase-space were given by Planck in the *Ann. d. Phys.* vol. 50 †. This structure depends on the integrals of the motion, and in $2f$-dimensional phase-space the elementary cell has, according to Planck, a volume equal to h^f where h is Planck's constant. Rules are also given depending on what Planck has called coherence or incoherence of coordinates which determine the splitting up of the single quantum condition respecting the volume of the cell into f different quanta conditions regarding the $f(q,p)$-planes.

In the next volume of the *Annalen* ‡ somewhat different and simpler conditions—and these are now largely accepted—are laid down by Sommerfeld. According to Sommerfeld the elementary volume $\int dq_1 dp_1 \ldots dq_f dp_f$ of phase-space may be regarded as determined by the f projections $\int dq_1 dp_1$, $\int dq_2 dp_2, \ldots \int dq_f dp_f$ on the $f(q,p)$-planes. Each of these integrals is then integrated with respect to p, and then he proceeds to write

$$\begin{aligned} \int p_1 dq - \int p_0 dq &= h, \\ \int p_2 dq - \int p_1 dq &= h, \\ &\cdots\cdots \\ \int p_n dq - \int p_{n-1} dq &= h, \\ \therefore \quad \int (p_n - p_0) dq &= nh. \end{aligned}$$

Assuming now that of the group of curves on the (q,p)-planes a path may be obtained such that $\int p_0 dq = 0$ along it, Sommerfeld gets the simplified form $\int p_n dq = nh$. For the limits of integration he gives the rule that it should be performed over that length of the orbit which brings up fresh phases in phase-space so that in periodic orbits the integration is over one complete cycle. In Newtonian orbits of the relativistic type or other quasi-periodic orbits where there is a regular forward motion (or backward) of

* Communicated by the Author.
† *Ann. d. Phys.* vol. l. p. 385 (1916).
‡ *Ann. d. Phys.* vol. li. p. 1 (1916).

the perihelion, this means a path of integration for $\int p_r dr$ from $r_{\min}$ to $r_{\min}$ through $r_{\max}$ or, what amounts to the same, double the path from $r_{\min}$ to $r_{\max}$. For the azimuthal phase-integral $\int p_\phi d\phi$ the path is taken to be just one complete cycle of 2π and not from $r_{\min}$ to $r_{\min}$ through $r_{\max}$. The reason for this variation as given by Sommerfeld seems to be that attention should be directed not so much to the actual orbit as to its counterpart in phase-space, and since an ellipse of a given size may have any position as regards the azimuth of its perihelion, and since the whole set of such ellipses should be taken into account, all phases are comprehended in a path of integration from 0 to 2π. The results obtained from these quanta conditions taken along with Bohr's famous rule for the frequency of the emitted radiation receive startling confirmation in the experimental results of Paschen * on the Balmer lines of hydrogen. The behaviour of the Rydberg number and of doublets and triplets is sufficiently near to the requirements of the formula.

It is at once possible, however, to raise certain theoretical objections to Sommerfeld's theory. In the first place, the elementary volume $\int dq_1 dp_1 \ldots . dq_f dp_f$, which I take to be equal to h^f after Planck, cannot be represented as

$$\int dq_1 dp_1 . \int dq_2 dp_2 . \int \ldots . \int dq_f dp_f .$$

This objection is met partly if, on the authority of Epstein and Schwarzschild—and to this Sommerfeld agrees,—the choice of the coordinates is determined by the possibility of separation of variables in the Hamilton-Jacobi equation. If such separation can be effected we should have according to Staeckel — at least in regard to a Staude-Staeckel dynamical system—p_i a function solely of q_i. The limits for $q_1, q_2, \ldots . q_f$ still remain interdependent, and this disposes of the possibility of the latter mode of representation even where the choice is made after the Epstein-Schwarzschild rule.

Secondly, the reasoning adduced by Sommerfeld in support of the path of integration for the azimuthal phase-integral $\int p_\phi d\phi$ appears to be far from convincing. It goes too far and would appear to indicate an identical path of integration for the phase-integral $\int p_r dr$. On the other hand, having in view the concepts of the time-total (Zeitgesamtheit) of phases and of the space-total (Raumgesamtheit)

* *Ann. d. Phys.* vol. l. p. 901 *et seq.* (1916).

of phases employed in statistical mechanics and the proposition that the time-total of phases of a single orbit is equal to the space-total of phases of all similar orbits *, we should rather have the path of integration extended over the complete orbit from r_{min} to r_{min} through r_{max}, seeing that although p_ϕ is constant the phase-point in phase-space does not come back to itself until starting from r_{min} we come back to r_{min} through r_{max}.

A third objection to Sommerfeld's treatment of the relativistic motion is that advanced by Planck † and Schwarzschild also in regard to the azimuthal phase-integral. According to Sommerfeld himself, the integral $\int dq dp$ is reducible to the form $\int p_n dq = nh$ only where a path may be obtained such that $\int p_0 dq = 0$ along it. This, however, is not possible owing to a minimum value of the angular momentum which cannot be passed if the elliptic motion is preserved. Planck himself, in his own treatment of the relativistic motion arrives at the result $2\pi(p_n - p_0) = nh$ as the azimuthal quanta condition where p_0 is the limiting value of the angular momentum. The behaviour of the Rydberg number in the experimental results of Paschen, however, tells against the form $2\pi(p_n - p_0) = nh$.

In the present paper I shall venture to suggest a fresh standpoint in regard to quanta conditions and to develop it by reference to the particular cases of (i.) the linear oscillator, (ii.) the rotator, (iii.) the ordinary Newtonian ellipse, and (iv.) the relativistic Newtonian ellipse. While they meet all the objections stated against Sommerfeld's theory, they give results identical with those of Planck and of Sommerfeld in the first three cases. The results obtained, however, in the case of the relativistic ellipses are at variance alike with those of Sommerfeld and of Planck as well as with those which Sommerfeld would have obtained if he had taken the path of integration for the integral $\int p_\phi d\phi$ as he appears at first to have done from r_{min} to r_{min} through r_{max}. The central idea in this investigation is still that of Planck, namely, the structure of phase-space must be on the basis of the integrals of the motion. As regards the experimental aspects of those conditions, I have to admit the disappearance of the doublets and the triplets; but the behaviour of the Rydberg number may be deemed to be sufficiently encouraging.

* *Repertorium der Physik*, Ganz u. Weber, p. 455.
† *Ann. d. Phys.* vol. l. p. 404 (1916).

§ 1. *One degree of freedom. Linear oscillator, rotator.*

We may state the quantum condition in the form

$$\int_0^n \int^{\circ} dt \delta H \quad \text{or} \quad \int_0^n T \delta H = nh,$$

where H is the energy and T is the periodic time *.

(a) *Linear oscillator.*

The equation of motion is $\ddot{x} + \mu^2 x = 0$; therefore $\dot{x}^2 + \mu^2 x^2 = \text{const.} = 2H$ (twice the energy) $= \mu^2 a^2$, where a is the amplitude. $T = \frac{2\pi}{\mu}$, therefore T is independent of H, μ^2 being an absolute constant. We therefore have $T(H_n - H_0) = nh$ or if $H_0 = 0$, $TH_n = nh$. In Planck's notation ϵ_n (the energy) $= \frac{nh}{T} = nh\nu$ (where ν is the frequency).

(b) *Rotator.*

The integral of energy is $\frac{1}{2}J\omega^2 = H$ (J being the moment of inertia and ω the angular velocity). $T = \frac{2\pi}{\omega} = \frac{\pi\sqrt{2J}}{H^{\frac{1}{2}}}$; $\therefore \int_0^n T\delta H = \int_0^n \pi\sqrt{2J} \cdot 2H^{\frac{1}{2}} = nh$; if $H_0 = 0$ we have $H_n = \frac{n^2h^2}{8\pi^2 J}$.

§ 2. *Two degrees of freedom. The ordinary Newtonian ellipse.*

We may state the quanta conditions in the forms $\int\int^{\circ} dt\,\delta H = nh$, $\int\int^{\circ} d\phi \delta p_\phi = n'h$, or in the alternative forms $\int_0^n T\delta H = nh$, and $\int_0^{n'} \Phi \delta p_\phi = n'h$ .... where p_ϕ is the angular momentum and Φ is the azimuthal period which in the present case is 2π.

The energy $H = -E = \frac{1}{2}\left\{ m(\dot{r}^2 + r^2\dot{\phi}^2) - \frac{2e^2}{r} \right\}$, and the angular momentum $= p = mr^2\dot{\phi}$.

* The symbol $\int^{\circ}$ is used throughout to mean integration over a complete circuit.

The periodic time

$$T = 2\int_{r_{min}}^{r_{max}} \frac{r\,dr}{\sqrt{\frac{2e^2}{m}r - \frac{p^2}{m^2} - \frac{2E}{m}r^2}} = \sqrt{\frac{2m}{E}}\int_{r_1}^{r_2} \frac{r\,dr}{\sqrt{(r_2-r)(r-r_1)}}$$

$$= \pi\sqrt{\frac{m}{2}}\cdot\frac{e^2}{E^{3/2}}\left[r_2 = r_{max.},\ r_1 = r_{min.}\right].$$

Therefore

$$nh = \int_0^n T\delta H = -\pi e^2\sqrt{\frac{m}{2}}\int_0^n \frac{\delta E}{E^{3/2}} = \pi e^2\sqrt{2m}\,E_n^{-\frac{1}{2}};$$

therefore $$H_n = -E_n = -\frac{2m\pi^2e^4}{n^2h^2},$$

which is in perfect accord with Sommerfeld's expression $-\frac{2m\pi^2e^4}{(n+n')^2h^2}$ if it is noticed that the single quanta number n really absorbs n' and stands for $n+n'$.

For the azimuthal phase-integral $\int_0^{n'}\Phi\,\delta p$ we have $2\pi p_{n'} = n'h$.

§ 3. *Theoretical considerations underlying the present mode of writing the quanta conditions.*

(i.) One degree of freedom; phase-integral :—

$$\int\int^{\infty} dt\delta H = h.$$

In integrating with respect to t over the whole period it is evident that we are taking account of all phases which a particular system passes through with constant energy, and in so doing we are also taking the space-total of all phases which systems with a given energy may have in phase-space. In subsequent integration with respect to H, therefore, we are accounting for the whole of phase-space corresponding to every variation of the energy. The elementary cell in this phase-space being equal to h, we have

$$\int\int^{\infty} dt\delta H \text{ or } \int T\delta H = h.$$

(ii.) Two degrees of freedom; ordinary Newtonian ellipse: phase-integrals $\int\int^{\infty} dt\delta H = h$;

$$\int\int^{\infty} d\phi\delta p = h.$$

What has been said respecting the case of one degree of freedom will apply equally well in this case to the phase-integral $\int\int\overset{\circ}{} dt\delta H$. But fresh phases come up by reason of the fact that keeping H and T constant we can vary p or the azimuth. The phases brought up by variation of azimuth have no necessary relation with those depending on time-difference, for T is a function of H while $\int\overset{\circ}{} d\phi$ is either an absolute constant or, as it is in the case of the relativistic ellipse, a function of p. Having regard, therefore, to the proposition that the space-total of phases of different systems having the same p, T, and H would be equal to the time-total of phases of a single system, we integrate $\int d\phi$ over the complete period. Subsequent integration with respect to p therefore accounts for all phases which can arise through these sources.

The observation may be made that the canonical coordinates $p_1 q_1$, $p_2 q_2$, etc. of a dynamical system are not unique and that it is easy to substitute for any pair (p, q) the pair (H, t). It is possible therefore to represent phase-space as determined by the system of coordinates $p_2 q_2, p_3 q_3, \ldots . H, t$. The elementary volume of this space in the present case would be $\int d\phi\, \delta p\, dt\, \delta H = \int d\phi\, \delta p \,.\, \int dt\, \delta H \ldots .$ because p and H are independent constants and Φ and T are functions of p and H respectively. This volume therefore is equal to h^2.

§ 4. *Possibility of reduction of the present quanta integrals to Sommerfeld's forms.*

Writing the Hamiltonian equations of motion in the bilinear form we have $\Sigma(dq\,\delta p - dp\,\delta q) = dt\,\delta H$ where d refers to a variation with time and therefore along the orbit, and δ refers to a variation independent of the time. In the present case

$$(dq_r\delta p_r - dp_r\delta q_r) + dq_\phi\delta p_\phi = dt\,\delta H, \text{ because } dp_\phi = 0.$$

Therefore $$\delta(p_r dq_r) - d(p_r\delta q_r) + dq_\phi\delta p_\phi = dt\,\delta H.$$

Integrating this form over a complete cycle we have

$$\delta\left[\overset{\circ}{\int} p_r dq_r\right] - \overset{\circ}{\left[} p_r\delta q_r\right] + 2\pi\,\delta p_\phi = T\delta H\ ^*;$$

* The symbol $\overset{\circ}{[\quad]}$ is used to mean the difference of values at the extremities of a complete circuit.

since $\overset{\circ}{[}p_r\delta q_r]$ is zero—and this may be easily verified—we may write

$$\delta\,[\overset{\circ}{\int} p_r dq_r] + 2\pi\,\delta p_\phi = \mathrm{T}\delta\mathrm{H}.$$

Integrating this equation between two orbits we have

$$[\overset{\circ}{\int} p_r dq_r]_1^2 + [2\pi\, p_\phi]_1^2 = \int_1^2 \mathrm{T}\delta\mathrm{H}.$$

It is now obvious that instead of associating a quanta number with the phase-integral $\int_1^2 \mathrm{T}\delta\mathrm{H}$ we may associate another with the integral $[\overset{\circ}{\int} p_r dq_r]_1^2$, which will be the difference of the quanta numbers associated with the former and with the expression $2\pi p_\phi$, and this is exactly what Sommerfeld has done.

§ 5. *Case of the relativistic ellipse; phase-integrals*

$$\iint dt\,\delta\mathrm{H} = nh, \quad \iint d\phi\,\delta p_\phi = n'h.$$

Sommerfeld writes for the equations of motion

$$\frac{d}{dt}(m\dot{x}) = -\frac{e^2}{r}\cos\phi, \quad \frac{d}{dt}(m\dot{y}) = -\frac{e^2}{r}\sin\phi,$$

where $m = m_0/\sqrt{1-\beta^2}$ and $\beta = \frac{v}{c}$.

Putting $\mathrm{K} = -m_0c^2\sqrt{1-\beta^2}$ we have

$$\frac{\partial \mathrm{K}}{\partial \dot{x}} = m\dot{x}, \quad \frac{\partial \mathrm{K}}{\partial \dot{y}} = m\dot{y}.$$

The equations of motion are therefore deducible from $\delta\int(\mathrm{K}-\mathrm{V})dt = 0$, where V is the potential $-\frac{e^2}{r}$. The angular momentum

$$\frac{\partial \mathrm{K}}{\partial \dot{\theta}} = \frac{m_0}{\sqrt{1-\beta^2}} r^2\dot{\theta} = mr^2\dot{\theta} = \text{const.} = p.$$

The energy

$$= \dot{x}\frac{\partial \mathrm{K}}{\partial \dot{x}} + \dot{y}\frac{\partial \mathrm{K}}{\partial \dot{y}} - \mathrm{K} + \mathrm{V} = \frac{m_0c^2}{\sqrt{1-\beta^2}} - \frac{e^2}{r} = \mathrm{H}\ (\text{constant}).$$

For the bilinear form of the Hamiltonian equations we proceed thus:—

Let $$\int_1^2 (\mathrm{K}-\mathrm{V})dt = \mathrm{S},$$

then

$$\delta S - \Big|_1^2 (K-V)\delta t = \Big|_1^2 \left\{ \frac{\partial K}{\partial \dot{x}} (\delta x - \dot{x}\delta t) + \frac{\partial K}{\partial \dot{y}} (\delta y - \dot{y}\delta t) \right\},$$

therefore $$\delta S = \Big|_1^2 (\Sigma p\, \delta q - H\delta t).$$

If d is a variation with time and therefore along the orbit, we have easily

$$(dq_r \delta p_r - dp_r \delta q_r) + dq_\phi \delta p_\phi = dt\, \delta H,$$

i. e. $$\delta(p_r dq_r) - d(p_r \delta q_r) + dq_\phi \delta p_\phi = dt\, \delta H.$$

Now the differential equation of the orbit has been deduced by Sommerfeld in the form

$$\frac{\partial^2 \sigma}{\partial \phi^2} + \sigma \left\{ 1 - \frac{e^4}{p^2 c^2} \right\} = \frac{m_0 e^2}{p^2} \left\{ 1 + \frac{H}{m_0 c^2} \right\},$$

and the equation to the orbit in the form $\sigma = A(1 + \epsilon \cos \gamma\phi)$,

where $$\sigma = \frac{1}{r}, \quad A = \frac{m_0 e^2}{p^2 \gamma^2} \left(1 + \frac{H}{m_0 c^2} \right), \quad \gamma^2 = 1 - \frac{e^4}{p^2 c^2}.$$

ϵ is given by the relation which is easily deduced,

$$1 + \frac{H}{m_0 c^2} = \sqrt{\frac{p^2 - p_0^2}{p^2 - \epsilon^2 p_0^2}}, \quad \text{where } p_0 = \frac{e^2}{c}.$$

The azimuthal period $= \frac{2\pi}{\gamma}$; therefore the phase-integral

$$\int_0^{n'} \oint dq_\phi \delta p_\phi$$

$$= \int_0^{n'} \frac{2\pi}{\gamma} \delta p = 2\pi \int_0^{n'} \frac{p \delta p}{\sqrt{p^2 - p_0^2}} = 2\pi \Big|_0^{n'} \sqrt{p^2 - p_0^2} \Big|,$$

$$\therefore \qquad 2\pi \sqrt{p^2 - p_0^2} = n'h.$$

For the phase integral $\int_0^n \oint dt\, \delta H$ we integrate the bilinear form over the whole orbit and obtain

$$T\delta H = \delta \left[\oint p_r dq_r \right] - \left[\oint p_r \delta q_r \right] + \frac{2\pi}{\gamma} \delta p.$$

But $\overset{\circ}{[}p_r\delta q_r] = \left[\frac{p}{m_0\sigma^2}\sqrt{1-\beta^2}\frac{\partial\sigma}{\partial\phi}\left\{-\frac{\delta A}{A^2(1+\epsilon\cos\gamma\phi)}\right.\right.$

$$\left.\left.-\frac{\delta\epsilon\cos\gamma\phi}{A(1+\epsilon\cos\gamma\phi)^2}+\frac{\epsilon\sin\gamma\phi}{A(1+\epsilon\cos\gamma\phi)^2}\cdot\phi\,.\,\delta\gamma\right\}\right]_0^{\frac{2\pi}{\gamma}}=0.$$

Therefore $\quad T\delta H = \delta\left[\overset{\circ}{\int} p_r dq_r + 2\pi\sqrt{p^2-p_0^2}\right],$

which shows that $T\delta H$ is an exact differential and T is a function solely of H.

Sommerfeld evaluates

$$\overset{\circ}{\int} p_r dq_r = 2\pi\sqrt{p^2-p_0^2}\cdot\left\{\frac{1}{\sqrt{1-\epsilon^2}}-1\right\}.$$

Therefore $\quad T\delta H = \delta\left[2\pi\sqrt{\frac{p^2-p_0^2}{1-\epsilon^2}}\right].$

But $\quad 1+\frac{H}{m_0c^2} = \sqrt{\frac{p^2-p_0^2}{p^2-\epsilon^2p_0^2}} = \sqrt{s}$ (say),

from which we obtain $\quad \frac{p^2-p_0^2}{1-\epsilon^2} = \frac{sp_0^2}{1-s}.$

Therefore

$$\int_0^n T\delta H = 2\pi\left(\frac{s_n p_0^2}{1-s_n}\right)^{\frac{1}{2}} = nh \quad (s_0=0, \text{ for the zero path}),$$

or $\quad 1+\frac{H_n}{m_0c^2} = \frac{nh}{\sqrt{n^2h^2+4\pi^2p_0^2}}.$

It will be seen that the energy thus depends on a single quanta number, and the doublets and triplets of the Balmer series would receive no explanation.

§ 6. *Comparison with the quanta propositions of Planck and Sommerfeld.*

Sommerfeld writes

$$2\pi\sqrt{p^2-p_0^2}\left\{\frac{1}{\sqrt{1-\epsilon^2}}-1\right\} = nh \quad \text{and} \quad 2\pi p = n'h,$$

while with Planck the latter would stand in the form

$$2\pi(p-p_0) = n'h.$$

According to Sommerfeld's original view of the path of integration for the azimuthal phase-integral the latter would stand in the form

$$\frac{2\pi p^2}{\sqrt{p^2-p_0^2}} = n'h.$$

All the azimuthal relations are therefore different from the relation $2\pi\sqrt{p^2-p_0^2} = n'h$ proposed in this paper, while if the present relation is admitted then the radial quanta number of Sommerfeld would appear to be the difference of the quanta numbers associated with the time-energy integral and with the azimuthal integral.

It is also obvious that

$$\int d\phi\,\delta p\,dt\,\delta \mathrm{H} = \int d\phi\,\delta p \,.\int dt\,\delta \mathrm{H},$$

since the period in ϕ is a function entirely of p, and the period in t that of H. Thus the elementary cell in phase-space has a volume equal to h^2. It will also appear that the least value of p, which is p_0, cannot be passed in quanta changes.

§ 7. *Comparison with Paschen's experimental results on the behaviour of the Rydberg number in the Balmer Series.*

We have $$\frac{\mathrm{H}_n}{m_0c^2} = \frac{nh}{\sqrt{n^2h^2+4\pi^2\frac{e_4}{c^2}}} - 1.$$

But $e = 4{\cdot}7.10^{-10}$; $h = 6{\cdot}5.10^{-27}$; $c = 3.10^{10}$

therefore $\frac{4\pi^2e^4}{c^2h^2}$ is of the order of 10^{-3}.

Therefore

$$\frac{\mathrm{H}_n}{m_0c^2} = \frac{1}{\left(1+\frac{4\pi^2e^4}{c^2n^2h^2}\right)^{\frac{1}{2}}} - 1$$

$$= -\frac{2\pi^2e_4}{c^2n^2h^2} + \frac{6\pi^4e^8}{c^4n^4h^4} - \text{ etc ;}$$

therefore

$$\frac{1}{\lambda}=\frac{\nu}{c}=\frac{H_n-H_{n'}}{ch}$$

$$=\frac{2\pi^2e^4m_0}{ch^3}\left(\frac{1}{n'^2}-\frac{1}{n^2}\right)\left\{1-\frac{3\pi^2e^4}{c^2h^2}\left(\frac{1}{n^2}+\frac{1}{n'^2}\right)+\ldots.\right\}$$

$$=N\left(\frac{1}{n'^2}-\frac{1}{n^2}\right)\left\{1-\frac{3\pi^2e^4}{c^2h^2}\left(\frac{1}{n^2}+\frac{1}{n'^2}\right)+\ldots.\right\},$$

where N is the Rydberg number.

The corrected Rydberg number N′ therefore for the hydrogen lines

$$=N\left\{1-\frac{3\pi^2e^4}{c^2h^2}\left(\frac{1}{2^2}+\frac{1}{n^2}\right)\right\}.$$

According to Sommerfeld

$$N'=N\left\{1+\frac{\pi^2e^4}{c^2h^2}\left(\frac{1}{2^2}+\frac{1}{n^2}\right)\right\}.$$

It will thus appear that the order of the correction here proposed, unlike that suggested by Planck, agrees with that of Sommerfeld's formula. There is however a difference in sign. However, if we observe Paschen's experimental values for H_α, H_β, H_γ, H_δ, which are as follow * :

	H_α.	H_β.	H_γ.	H_δ.
N′	109678·205	109678·164	109678·167	109678·198

it will be noticed that apart from H_α the successive numbers show an increase and not a decrease, and this fact is in harmony with the formula here proposed rather than with Sommerfeld's form which by making ΔN positive would cause N to decrease down the series.

§ 8. *Conclusion.*

The extension of the theory of the present paper to a case of n degrees of freedom may be made provided we have the n first-integrals of the motion of which one is necessarily the integral of energy. When the positional coordinates, which are canonical conjugates of the integration-constants treated

* *Ann. d. Phys.* vol. l. p. 935 (1916).

as momenta, are obtained, the quanta-integrals may be written in the forms

$$\int_0^n \mathrm{T}\delta\mathrm{H} = nh, \quad \int_0^{n'} \Phi\, \delta p_\phi = n'h, \quad \int_0^{n''} \Psi \delta p_\psi = n''h, \text{ etc.},$$

T, Φ, Ψ, etc. being the periods of the system with respect to such positional coordinates.

It is evident that a quanta integral would tend to become infinite if the periodic time or the period of the positional coordinate is infinite, *i. e.* if the dynamical system in respect of that particular coordinate is not periodic. It would thus follow that quantaic changes of energy or momenta are a property of periodic or quasi-periodic motions and that where there is no periodicity the energy changes or momenta changes must be gradual—a fact which will ensure a finite value for the quanta-integral.

Summary.

In this paper the suggestion has been made on theoretical grounds of statistics that the quanta integral in the case of one degree of freedom should be written in the form

$$\int_0^n \mathrm{T}\delta\mathrm{H} = nh,$$

and that in the case of Newtonian elliptic motion both of the ordinary and the relativistic type quanta integrals should be written in the forms

$$\int_0^n \mathrm{T}\delta\mathrm{H} = nh, \quad \int_0^{n'} \Phi\delta p = n'h$$

(where T is the periodic time, H the energy, Φ the complete azimuthal period, and p the angular momentum). The consequences of this theory are compared with those of Sommerfeld's and with the observations of Paschen on the Balmer lines of hydrogen, and it is shown that while the doublets and triplets receive no direct explanation, there being no splitting of energy as with Sommerfeld, the behaviour of the Rydberg number may be regarded as somewhat more satisfactory.

LXII. *The Meaning of "a" and "b" in the Equation of State.* *By* Angus F. Core, *Chemical Department, University of Manchester* *.

IN the second part of a paper entitled "Notes on the Kinetic Theory of Gases" (Phil. Mag., May 1922) Mr. Fowler calculates the value of van der Waals' "*a*." There seems to me to be something unsatisfactory in taking the "*a*" that he finds to correspond to the "*a*" of van der Waals' equation of state. This equation may be written in the form

$$pv = \mathrm{RT} + \mathrm{RT}b/v - a/v$$

when the gas is moderately rarefied. The general virial equation so far as the second virial term is $pv = \mathrm{RT} + \mathrm{B}/v$. Now except under certain conditions, even when the molecules contain perfectly hard kernels, the term B/v does not naturally fall into two parts corresponding to $\mathrm{RT}b/v$ and a/v, that is into two parts one of which is proportional to the temperature and the other independent of the temperature. Therefore, in order to separate B/v into two parts it is necessary to define either "*a*" or "*b*."

When the molecules have perfectly hard kernels, then $\mathrm{RT}b/v$ may be defined as that part of the virial due to the forces that arise when the kernels actually collide. If σ is the diameter of the kernels and $-\chi(\sigma)$ the work required to separate to infinity two molecules in contact, then, as Reinganum showed, this collision virial equals

$$\frac{2\pi \mathrm{N}\sigma^3}{3v} e^{-\frac{\chi(\sigma)}{k\mathrm{T}}}.$$

The rest of the virial

$$\frac{\mathrm{B}}{v} - \frac{2\pi \mathrm{N}\sigma^3}{3v} e^{-\frac{\chi(\sigma)}{k\mathrm{T}}},$$

may be called $-a/v$, but this does not mean that the "*a*" so defined corresponds satisfactorily with the "*a*" of van der Waals.

B/v can, however, be separated into two parts by defining the meaning of "*a*." Thus a/v may be defined as half the work required to abstract N molecules chosen at random from the interior of the gas to infinity outside the gas. This definition is, however, ambiguous. The ambiguity is removed by stating that when a molecule is being removed the other molecules are to be considered fixed in position.

* Communicated by Prof. A. W. Porter, F.R.S.

The work done on a molecule then gives the change in the potential of the molecule usually referred to as χ; and the work for the N molecules will give the increase in potential energy consequent on the removal of one gram molecule from the interior of a vessel filled with the gas. Minus half this quantity, that is $-a/v$, is the potential energy of a gram molecule of the gas. To the same degree of approximation as results from the neglect of all the virial terms beyond the second, "a" is independent of v. Therefore

$$\frac{a}{v} = -\, v \frac{d\,\frac{a}{v}}{dv}.$$

According to the classical kinetic theory the kinetic energy is constant so long as the temperature is constant, so that if U is the total energy of the gas per gram molecule

$$\frac{a}{v} = v\left(\frac{\partial \mathrm{U}}{\partial v}\right)_{\mathrm{T}}.$$

Therefore

$$\frac{a}{v} = v\left(\mathrm{T}\left(\frac{\partial p}{\partial \mathrm{T}}\right)_{v} - p\right).$$

This allows a/v to be calculated when the equation of state is known. Expressed directly in terms of the molecular field, the potential energy per gram molecule is given by

$$-\frac{a}{v} = \frac{2\pi \mathrm{N}^2}{v}\int_0^{\infty} r^2 \chi e^{-\frac{\chi}{k\mathrm{T}}} dr$$

in which χ is the potential of a molecule at a distance r from the centre of another molecule.

It is the a/v thus defined that corresponds most closely with the a/v of the equation of van der Waals. The remaining part of the second virial term may be called $\mathrm{RT}b/v$. This cannot be called the collision virial, for when the molecules contain a hard kernel it does not in general reduce to the collision virial of Reinganum. Perhaps the best name for the two parts of the second virial term as defined above are the potential part and the non-potential part.

a/v may, however, be defined as half the work required to remove N molecules chosen at random when, during the removal, the other molecules are allowed to move into their new positions of statistical equilibrium, the volume of the gas being kept constant. This work does not equal the increase

of potential energy, and is usually less. If carried out under isothermal conditions there will be an exchange of heat with the surroundings. When the gas is sufficiently rarefied so that the variation in density towards the boundary can be neglected, then $-a/v$ thus defined must equal the entire term B/v.

When the molecules contain a hard kernel we may modify this definition of a/v by excluding from this term that part of the work done by the impulse forces arising on collision. This, in effect, is what Mr. Fowler does. But even then this remaining work does not give the increase in potential energy consequent on the removal of the molecules.

The division of the term B/v which follows from this definition of a/v must be the same as that of Reinganum, for the other part of the term—that is RTb/v, is due to the collision impulses.

This method of division, apart from the fact that it is only applicable when the kernels are perfectly hard, may give rise to a separation which has very little significance. Suppose, for example, that the field of the molecule consists of an inner spherical region of radius σ throughout which the potential is infinite, surrounded by a shell of thickness d across which the potential rises from $\chi(\sigma)$ on the surface just outside the inner region to zero on the outer surface. The collision virial is equal to

$$\frac{2\pi N\sigma^3}{3v} e^{-\frac{\chi(\sigma)}{kT}},$$

whatever be the value of d. If d is made indefinitely small the total virial must be $\frac{2\pi N\sigma^3}{3v}$, for the molecules are indistinguishable from simple hard spheres of diameter σ. Therefore, if we insist on making the collision virial correspond to RTb/v, the value of a/v must be

$$\frac{2\pi N\sigma^3}{3v}\left(e^{-\frac{\chi(\sigma)}{kT}}-1\right).$$

But it is evident that, the molecule now being a hard sphere without external field, the proper value of the a/v of van der Waals is 0, and that of RTb/v is $\frac{2\pi N\sigma^3}{3v}$.

The University, Manchester,
September 1922.

LXIII. *On the Molecular Scattering and Extinction of Light in Liquids and the Determination of the Avogadro Constant.* *By* C. V. Raman, *M.A., Hon. D.Sc., Palit Professor of Physics in the Calcutta University, and* K. Seshagiri Rao, *M.A., University of Madras Research Scholar* *.

1. *Introduction.*

THE phenomena of molecular scattering of light in liquids are of great interest from several different points of view. Apart from the importance they possess as an illustration of optical theory, their study throws light on fundamental problems concerning the nature of the liquid state and the anisotropic structure of atoms and molecules. They are also concerned in the explanation of one of the most beautiful of natural phenomena, that is, the colour of the deep sea and of other large masses of clear water, as has been explained by one of us in a recently published book †. It may also be pointed out that the molecular scattering of light in the oceanic waters contributes in a noticeable degree to the albedo of the earth and thus possesses an astronomical significance. It is proposed in this paper to discuss in detail the theory of molecular diffraction in liquids and to describe further experimental work on the subject.

2. *Einstein-Smoluchowski Formula.*

A suggestion has been made by some previous writers ‡ that the Rayleigh law of scattering according to which the fraction of the incident energy that is laterally scattered in passing through a unit volume of the substance is

$$\frac{32\pi^3(\mu-1)^2}{3n\lambda^4}, \quad \ldots \ldots \quad (1)$$

applies also to liquids. *This is not true.* The assumption on which the law of scattering stated in (1) is derived, namely, that the scattered waves arising from the individual molecules arrive in arbitrary phases at the point of observation, is certainly not applicable in the case of condensed media, as

* Communicated by the Authors.

† 'Molecular Diffraction of Light,' Calcutta University Press, February 1922. See also 'Nature,' Nov. 24, 1921, and "The Molecular Scattering of Light in Water and the Colour of the Sea," Proc. Roy. Soc. April 1922.

‡ F. E. Fowle, Astrophysical Journal, vol. xxxviii. p. 392 (1913); Cabannes, *Ann. de Phys.* tome xv. pp. 1–150 (1920).

was indeed pointed out by the late Lord Rayleigh himself. The molecules in such a media are within each other's sphere of action practically all the time, and their ordering in space is therefore very far indeed from being a random arrangement. The relative phases of the scattered waves from the individual molecules are hence not uncorrelated, and we cannot expect the fraction of the incident energy which appears as scattered light to be given by (1).

A more promising method of approach for dealing with the problem of molecular scattering of light in liquids is the "Theory of Fluctuations" developed by Einstein and Smoluchowski, of which a discussion has been given in the paper on molecular scattering in dense vapours and gases *. According to this theory, the fraction of the incident energy which is scattered in passing through unit volume of fluid is

$$\frac{8\pi^3 RT\beta(\mu^2-1)^2(\mu^2+2)^2}{27N\lambda^4}, \quad . \quad . \quad . \quad . \quad (2)$$

where β and μ are respectively the compressibility and refractive index of the fluid, T is the absolute temperature, λ is the wave-length of the incident light, R is the gas-constant, and N the Avogadro number, both the latter referring to a gram-molecule. According to this theory, the light scattered by a liquid in a direction transverse to the primary beam should be completely polarized. It has been already pointed out by one of us † that the intensity of the transversely scattered light is correctly given by the Einstein-Smoluchowski formula in the case of those liquids in which its polarization is tolerably complete. In the case of many liquids, however, a very considerable admixture of unpolarized light appears, and we have now to consider the explanation of this fact and the modification of the theory that it necessitates.

3. *Imperfect Polarization of Transversely Scattered Light in Liquids.*

As already explained in the paper on scattering in dense vapours and gases, the Einstein-Smoluchowski theory is based on purely thermodynamic conceptions and practically does not consider the molecular structure of the fluid at all. It, in fact, regards a fluid as a continuous medium which is, however, subject to local fluctuations of density, and makes

* C. V. Raman and K. R. Ramanathan, Phil. Mag. January 1923.
† *Loc. cit.*

use of the Lorentz-Mosotti relation connecting changes of refractive index with the density to evaluate the intensity of the scattered light. If, however, we consider the subject from a molecular standpoint, the same result as that contained in the Einstein-Smoluchowski formula would be obtained, provided it be assumed that the molecules are isotropic. In the general case of a liquid consisting of anisotropic molecules, we may divide the effect to be expected into two parts : (*a*) a part due to the thermal fluctuations of density, and (*b*) a part due to the anisotropy and varying orientations of the molecules. We may assume without appreciable error that part (*a*) would be quantitatively determined by the Einstein-Smoluchowski theory, and that this part of the scattered light observed transversely to the primary beam would be completely polarized. From general considerations it would appear that part (*b*) should consist almost entirely of unpolarized light having an equal intensity in all directions. For, in an ordinary liquid, the molecules do not tend to set themselves definitely in any particular direction, and though in the case of molecules possessing permanent electrical or magnetic moments, a mutually directive influence may be perceptible, the molecules in any appreciable volume of the liquid find themselves, on the average, in all possible orientations relatively to the direction of the incident light vector. Hence the light vector in part (*b*) lies mostly in all possible orientations. However, to be quite accurate, we may assume that part (*b*) also includes a certain proportion of polarized light, and proceed to find the increase resulting therefrom in the intensity of the transversely scattered light. Assuming the incident and scattered beams to lie in a horizontal plane and the former to be unpolarized, we may write down the expressions for the intensity of the vertical and horizontal components in the scattered beam. The intensity of the vertical component is $\Omega_0+\epsilon\Omega_1+2\Omega_1$ and of the horizontal component is $2\Omega_1$, where Ω_0 is the contribution arising from density fluctuations and Ω_1 that arising from molecular anisotropy, of which the polarized part $\epsilon\Omega_1$ appears only in the vertical component. The unpolarized part Ω_1 appearing both in the horizontal and vertical components is multiplied by the factor 2 in each case as it arises in equal proportions from the vertical and horizontal components of the *incident light.*

The ratio of the intensities of the horizontal and the vertical components is thus

$$\frac{2\Omega_1}{\Omega_0+\epsilon\Omega_1+2\Omega_1}=\rho \text{ (say)}, \quad . \quad . \quad . \quad . \quad (3)$$

and the total intensity is

$$\Omega_0+\epsilon\Omega_1+4\Omega_1, \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

which may be written in the form

$$\Omega_0 \cdot \frac{6+6\rho}{6-(6+3\epsilon)\rho}. \quad . \quad . \quad . \quad . \quad . \quad (5)$$

The intensity of the light transversely scattered is thus greater than that indicated by the Einstein-Smoluchowski formula in the ratio

$$\frac{6+6\rho}{6-(6+3\epsilon)\rho}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

We have now to determine the values of ρ and ϵ in the case of liquids. The case of gases with anisotropic (ellipsoidal) molecules has been investigated by the late Lord Rayleigh, who has shown that if A, B, C are three parameters expressing the light-scattering power of a molecule for three mutually perpendicular directions of vibration fixed in it, the ratio of the intensities of the weaker and stronger components of the transversely scattered light is

$$\rho=\frac{2(A^2+B^2+C^2-AB-BC-CA)}{4(A^2+B^2+C^2)+AB+BC+CA}. \quad . \quad . \quad (7)$$

The total intensity is proportional to

$$\tfrac{1}{15}[6(A^2+B^2+C^2)-(AB+BC+CA)]. \quad . \quad . \quad (8)$$

Since $(\mu-1)^2$ for the gas is proportional to $(A+B+C)^2$, it may easily be shown by eliminating A, B, and C with the aid of (7), as has been done by Cabannes, that the actual intensity of scattering given by (8) is greater than for a gas of equal refractivity having isotropic molecules in the ratio

$$\frac{6(1+\rho)}{6-7\rho}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

In order that our formula (6) may be applicable generally (that is, both for liquids and gases) it must reduce to (9) in the case of gases, and this will be so provided $\epsilon=\frac{1}{3}$. This value of ϵ (that is, the proportion of polarized to unpolarized light in the additional scattering due to molecular anisotropy) agrees with the result of an investigation by Born * for the cases of gases with anisotropic molecules, and since,

* *Verh. Deutsch. Phys. Gesell.* vol. xix. p. 243 (1917); vol. xx. p. 16 (1918).

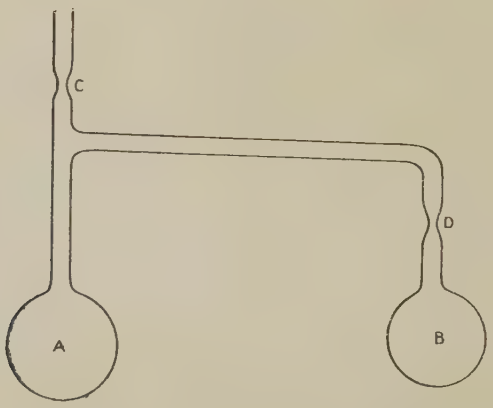
in any event, its influence is small, as may be seen from (4), we may at least tentatively take $\epsilon = \frac{1}{3}$ generally. The actual intensity of transverse scattering is thus greater than the scattering given by the Einstein-Smoluchowski formula in the ratio $\frac{6(1+\rho)}{6-7\rho}$. We shall refer to this multiplying factor in future as the Cabannes correction. The value of ρ, as can be seen from (3) and (4), depends on the relative magnitudes of Ω_0 and Ω_1, that is, on the relative importance of density fluctuations and of anisotropy in the total light-scattering, and will thus vary considerably with the condition of the substance. In a gas obeying Boyle's law, both the position and orientations of the molecules may be taken to be absolutely at random, and the intensity of both types of scattering is in proportion to the density of the gas. The state of polarization of the light scattered by a gas or vapour obeying Boyle's law does not therefore depend on its density or temperature. The case is, however, altered when the conditions are such that there are considerable deviations from Boyle's law, or when the substance is in the state of liquid. *In liquids under ordinary conditions*, owing to the very small value of the compressibility, the scattering due to density fluctuations is considerably less than in proportion to the density of the liquid. The scattering due to the anisotropy of the molecules, on the other hand, would be simply proportional to the number of molecules per unit volume: that is, to the density, *provided we assume that in the liquid state the molecules are oriented at random and their mutually directive influences do not exercise any sensible effect.* It follows from (3) that the proportion of the unpolarized to the polarized part in the light scattered by a liquid would therefore be much greater than for the same substance in the condition of vapour at ordinary pressure. The state of affairs, on the other hand, is reversed when we consider a liquid at higher temperatures and pressures approaching the critical condition, when the scattering power given by the Einstein-Smoluchowski formula is *greater* than in proportion to the density. The ratio of the unpolarized to the polarized part would then be *smaller* than for vapours at ordinary pressures. In any case, the percentage of unpolarized light may be calculated theoretically for any arbitrary condition of temperature and pressure on the basis of the assumption referred to, when it is known for one particular case, *e. g.*, for the state of rarefied vapour. In the case of a gas or vapour the maximum value of ρ is $\frac{1}{2}$, corresponding to the case of a linear molecule. In the case of a

liquid the maximum value of ρ is $\frac{6}{7}$, which is only reached when the scattering due to density fluctuations is altogether negligible in comparison with that due to orientation fluctuations. If $\epsilon = 0$, then ρ may have any value up to unity.

4. *Observations of Light Scattering in Liquids.*

In the paper on "The Colour of the Sea" *, some observations on the intensity and polarization of comparatively mote-free water obtained by simple distillation and settling have already been described. For a more careful quantitative examination, liquids purified by repeated slow distillations *in vacuo* may be used. A convenient form of apparatus for this purpose has been described by W. H. Martin †. A bulb of the form shown in fig. 1 may be used.

Fig. 1.



A quantity of the pure liquid under examination is introduced through C into the bulb A, and the vessel is then exhausted and sealed off at C. Warming up A a little and lowering the temperature of B, the liquid distils over into the latter, and in order to cleanse it thoroughly, the distillate is rinsed back into A several times. The fourth or fifth distillate, if considered satisfactory, is retained in the bulb B, which is then sealed off at D and detached. If the bulb

* Proc. Roy. Soc. April 1922; see also 'Molecular Diffraction of Light,' *loc. cit.*

† Journal of Physical Chemistry, xxiv. (1920) p. 478 and Jan. 1922.

be now placed in the path of a narrow cone of sunlight from a condensing lens which is focussed at its centre, the brilliant blue track of the beam in the liquid can be easily seen. In order to avoid the effect of stray light reflected from the sides of the bulb, it may be painted dead black outside, or in the alternative be immersed in a large beaker containing clear distilled water, which is painted dead black outside, openings being left for admission and exit of the beam and observation of the scattered cone of light passing through the liquid. The intensities of the scattered light from different liquids may be accurately compared with each other or with that in ether vapour saturated at room-temperature by a photographic method. The tracks are photographed side by side with equal exposures on a plate, the aperture of the camera-lens being varied by trial so as to obtain a record with the same degree of blackening. The ratio of the apertures gives immediately the ratio of the intensities. Since the scattering power of ether vapour at ordinary temperature is known absolutely from the experiments of Lord Rayleigh, the observations enable a comparison to be made of the scattering power of the liquid with the theoretical value indicated by the Einstein-Smoluchowski formula with the Cabannes correction.

The degree of polarization of the scattered light may be easily determined visually with the aid of a double-image prism and a nicol. The double-image prism gives two images of the track polarized respectively in horizontal and vertical planes, and by rotating the nicol placed behind it, two positions may be found in which the images appear of equal intensity. If 2θ be the angle between these two positions of the nicol, then, obviously, $\rho = \tan^2\theta$. By inserting in the path of the cone of the sunlight before it enters the bulb one or other of a succession of Wratten colour filters transmitting restricted regions of the spectrum, the dependence of the degree of polarization on the wavelength of the scattered light has been studied.

5. *Some Experimental Results.*

The results shown in Table I. illustrate the agreement of the observed light scattering power of liquids with that calculated from the theoretical considerations set out in articles 2 and 3. The observed data relate to the integrated effect of the whole spectrum when colour filters were not used.

TABLE I.

Liquid.	Mean refractive index μ.	Compressibility $\beta \times 10^6$ per atmosphere.	$\rho =$ weak comp. / strong comp. of polarization.	Cabannes factor $\frac{6(1+\rho)}{6-7\rho}$.	Observed scattering power in terms of pure air at N.T.P.	Calc. value.
			Per cent.			
Water	1·337	42	12·5	1·30	165	177
Ether.....	1·358	200	8·3	1·19	860	926
Methyl alcohol	1·333	130	15·1	1·39	495	560
Ethyl alcohol	1·366	120	13·0	1·33	620	653
Benzene	1·510	100	39·8	2·62	3135	2861
Chloroform ...	1·450	145	15·0	1·39	1567	1503
Carbon tetrachloride	1·467	100	11·0	1·27	1040	1056
Toluene	1·510	110	40·0	2·73	2970	3146
Carbon bisulphide ...	1·650	104	70·0	9·27	16000	23120

The general agreement is satisfactory, any discrepancies noted being in all probability due to uncertainty in the value of the compressibility β of the liquid, except in the case of carbon disulphide for which we get a better result if in (3) and (4) ϵ is taken as zero.

6. *Dependence of Polarization and Intensity on the Frequency of the Light.*

In several liquids studied, a distinct dependence of the value of ρ (the ratio of the weak to the strong component of polarization) on the frequency of light was found. The results are shown in Table II.

This observed dependence of the state of polarization of the scattered light on its frequency is very important, as it indicates that the molecular anisotropy indicated by the experiment is connected with the optical resonance frequencies of the molecules.

The dependence of the intensity of the scattered light on the frequency is determined by three factors. The first is the λ^{-4} law, which is obviously the most important and determines the blue colour of the scattered light. Then again the refractive index μ of the liquid which appears in

the formula is not independent of the wave-length, and in the case of highly dispersive liquids, its variation would not have a negligible influence. Finally, since ρ depends on the wave-length, the Cabannes correction which, as we have seen,

TABLE II.

ρ expressed in percentages.

Liquid.	Mean value of ρ for whole spectrum.	Value of ρ.				
		Red.	Yellow.	Green.	Blue.	Violet.
	Per cent.					
Water ...	12·5	9·4	10·6	10·7	15·5	21·0
Ether	8·3	8·2	8·2	8·2	9·0	9·2
Methyl alcohol	15·1	12·5	12·6	12·6	15·0	17·2
Ethyl alcohol	13·0	10·9	10·9	10·9	13·0	15·0
Benzene ...	39·8	39·8	39·8	39·8	41·0	41·0
Toluene ...	40·0	40·0	40·0	40·0	40·0	40·0

is of great importance in the case of liquids, would vary with the frequency in a manner characteristic of the liquid. Thus we cannot expect the ratio of intensities of the scattered light to the incident light to vary exactly in inverse proportion to the fourth power of the wave-length. This is no doubt the explanation of the fact that the colours of the track of the primary beam in different liquids do not exactly match each other, even when the intensities are equalized by altering the apertures.

7. *Dependence of Intensity and Polarization on Temperature.*

From the Einstein-Smoluchowski formula, it is clear that the scattering power of a fluid is proportional to the absolute temperature T, and it is also influenced by the changes of the refractive index and the compressibility β, which are both functions of temperature. In general, as the temperature rises, the density and therefore also the refractive index diminishes and the compressibility increases. The influence of the latter usually preponderates, with the result that increase of temperature generally means a considerable increase in the scattering power of the liquid. In special

cases, *e. g.*, water, where the compressibility shows a fall with rising temperature, a moderate increase of temperature should not produce much effect, but ultimately here as well a sufficient increase of temperature must result in an increased scattering. As the critical temperature of the substance is approached, the compressibility increases rapidly and ultimately becomes very large, and the scattering in the liquid becomes very great, giving rise to the well-known opalescence observed under the critical conditions. This increase in scattering may be very readily observed by putting the liquid in a strong sealed bulb and placing it in an enclosed electrical heater provided with suitable windows for ingress and egress of the illuminating pencil and for observation of the scattered light. Studies of this kind have been carried out by other workers in the author's laboratory for a number of liquids (ether, benzene, pentane, etc.) over a large range of temperatures, and the results together with a discussion are being published in separate papers. In the case of liquid ether, the increase in scattering with the rise and its decrease with the fall of temperature may easily be demonstrated by immersing the bulb in a beaker of hot water or in a Dewar flask containing a suitable cooled liquid. As an instance of the effects observed may be mentioned some measurements made with ether at 0° C. and 60° C. The ratio of the scattering powers at these temperatures was observed and found to be 1·60. The compressibility increases from 160×10^{-6} to 300×10^{-6} and the refractive index falls from 1·370 to 1·334, and the ratio of the scattering powers at these temperatures indicated by the Einstein-Smoluchowski formula is 1·41, showing a fair agreement with observation.

It is important to notice that the state of polarization of the scattered light also alters considerably with change of temperature. The quantity ρ and the Cabannes factor $\frac{6(1+\rho)}{6-7\rho}$ are thus both functions of temperature. That this is to be expected has already been pointed out in Art. 3, inasmuch as the scattering Ω_0 due to density fluctuations follows the Einstein-Smoluchowski formula and thus increases with rise of temperature, while the scattering $\frac{13}{3}\Omega_1$ due to anisotropy should (on the assumption of purely random orientation of the molecules) be proportional to the density, and thus actually diminish with the fall of temperature. Actually, by working with sealed tubes, the changes in the polarization of the light scattered both by liquids and

by vapours have been studied, and it has been found in general agreement with the theory that the polarization becomes more and more nearly perfect as the critical temperature is approached. It does not fall within the scope of this paper to go more fully into the experimental details on this point, but it is worth while here to draw attention to the question how far the relation between the value of ρ for the vapour and for the liquid obtained on the assumption that the molecules are oriented absolutely at random in both cases, and that the mutual *orienting* influence of the molecules is negligible, is in agreement with facts.

TABLE III.

ρ is expressed in percentages.

Liquid.	Observed value of ρ in vapour.		Calc. value of ρ for liquid.	Obs. value of ρ for liquid.
	Rayleigh.	Authors.		
			Per cent.	Per cent.
Ether	1·7	1·7	10·9	8·3
Benzene	6·0	7·0	40·0	39·8
Chloroform ...	3·0	3·0	18·2	15·0
Carbon tetrachloride	3·2	3·0	27·7	11·0
Carbon bisulphide ...	12·0	?	45·0	70·0

The values of ρ in the state of vapour for the substances shown in Table III. have been given by Lord Rayleigh as determined by a photographic method. They have been redetermined by the authors by a direct *visual* observation of the track of a concentrated beam of sunlight in respective vapours contained in a cross tube, a nicol and double-image prism being used. The value of ρ for carbon bisulphide vapour is marked by Lord Rayleigh as doubtful, owing to the formation of cloud. The experimental value of ρ for the different liquids is given as determined by the authors at ordinary temperatures (35° C.). It will be seen in the case of benzene that there is a fairly good quantitative agreement between theory and observation. In the other cases the agreement is only qualitative, showing that the assumption of absolutely random orientation of the molecules in the

liquid and gaseous states and neglect of their mutual orienting influence is not fully justified. The fuller explanation of these discrepancies and of their changes at different temperatures is a matter for further investigation.

8. *Relation between Polarization of Scattered Light and Dispersion Formulæ.*

That the degree of optical anisotropy of the molecule may depend on the frequency of the incident light has been suggested by a number of writers, including the late Lord Rayleigh *, and as we have seen above, the examination of molecular scattering of light in liquids furnishes evidence that this is actually the case. Formulæ have been suggested connecting the degree of imperfection of the polarized light with the resonance frequencies of the molecules in different directions. Recently Havelock † has attempted, apparently with success, to pursue the matter further by utilizing the empirical dispersion formulæ for this purpose and has dealt with the case of hydrogen. It is obvious that the method may be extended further, and that the data made available by the observation of the authors on liquids with different wave-lengths enables a closer test to be made of the idea. We propose to deal with this more fully in a separate paper.

9. *Molecular Extinction of Light in Liquids.*

From the Einstein-Smoluchowski formula it follows that the intensity of a beam of light traversing a liquid would diminish owing to the scattering of light according to the formula

$$I = I_0 e^{-\alpha l},$$

where

$$\alpha = \frac{8\pi^3}{27} \frac{RT\beta(\mu^2-1)^2(\mu^2+2)^2}{N\lambda^4}.$$

This formula, however, requires correction for the effect of molecular anisotropy and will only be valid for those parts of the spectrum for which the liquid exercises no selective absorption, and it also assumes that the liquid contains no suspended matter. It has already been pointed out in a note in 'Nature,' that the corrected formula agrees with the experimental result obtained by Martin for dust-free benzene for wave-lengths 5461 and 4358 A.U. The determination of the extinction coefficient for other wave-lengths and for

* Born, *Verh. Deutsch. Phys. Gesel.* xvi. (1918) and see also *Zeit. für Physik*, xxxvii. (1921); and J. J. Thomson, Phil. Mag, xl. (1920).

† Proc. Roy. Soc. May 1922.

other liquids (for which the coefficient is much larger than in water) should not present serious difficulties. Even with relatively short columns by the use of photo-electric cells balanced against one another, small extinction-coefficients should be capable of being determined with accuracy. Experimental work on this point is now in progress in the authors' laboratory.

10. *Absolute measurements and the Determination of the Avogadro Constant.*

Cabannes * has determined the Avogadro constant by means of absolute determination of the light-scattering in gases. Since the Einstein-Smoluchowski formula for the scattering of light in fluids contains the Avogadro number (the other quantities μ, T, R, β, and λ being known), the Avogadro constant may also be determined by observations on light-scattering in liquids. This has been done by the writers in the following way.

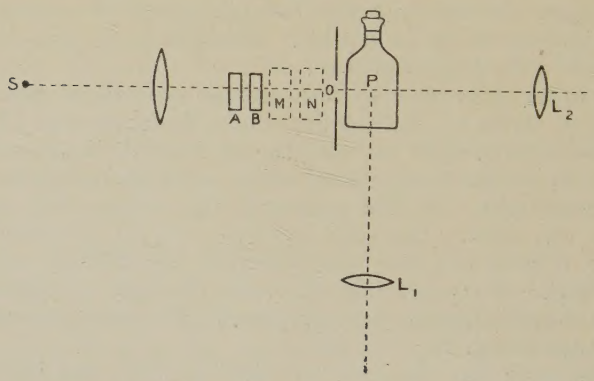
In order to be able to measure the amount of scattered light in terms of the incident light, it is necessary to use monochromatic light and also to cut down the incident light so as to enable comparisons to be made between it and the scattered light. As the source of light a mercury arc in silica was used. The 4358 line was used, all the other lines being filtered out by cuprammonium and quinine sulphate solutions. For reducing the incident light a solution of potassium dichromate was prepared. The arrangement was as shown in fig. 2.

The water that was used was distilled water that had been allowed to stand for a long time in a plane-sided glass bottle. The water was very clear, the motes all having settled down. The track when illuminated by a concentrated beam of sunlight was a fine blue one showing practically no motes. It was dead-blacked on all sides excepting apertures for ingress and egress of light, and observation of the track. The light from the arc S was focussed by a lens on the bottle through a rectangular aperture O. A and B were cells containing cuprammonium and quinine sulphate, respectively, to filter out the 4358 radiation. A square-sided bottle M contained the absorbing solution of potassium dichromate. The strength of the solution was varied by trial till the incident light was reduced in the proper ratio, such that its brightness was quite comparable with that of the track. To ensure that all the longer wave-lengths, 4916 etc.,

* *Ann. de Physique*, tome xv. (1920).

were absolutely cut off, another cell N containing a strong solution of cuprammonium was placed in the path of the incident beam. Wave-lengths smaller than 4358 had been initially cut off by the quinine sulphate solution, and the potassium dichromate solution reduces them further more equally well with the 4358 line. Thus it was ensured that both the reduced incident light and the scattered light were strictly of the same wave-length, a condition which is absolutely necessary since the intensity of the scattered light varies as λ^{-4}. The method of comparison consisted in photographing the track at P by means of a lens L_1, at a definite distance r from the track, and in photographing the incident light at P by the same lens at L_2 and at the same distance r. When photographing the incident beam the

Fig. 2.



absorbing solutions M and N were placed in position to cut down the incident light. Photographs of both were taken on the same plate, the time of exposure being the same, and the final adjustments for the equality of the two tracks being made by altering the aperture of the lens L. The absorption of the solutions was determined accurately by means of a Nutting photometer, using a cell of a centimetre thickness to contain the solution. In calculating the total absorption, a correction for the reflexions at the glass surfaces of the cell and the bottle was made. The ratio thus obtained had to be further corrected owing to the fact that the incident light was slightly converging, while the diffused light is scattered in all directions. According to the Einstein-Smoluchowski formula, the total amount of light scattered in all directions is

$$\frac{8\pi^3}{27}\frac{\mathrm{RT}\beta(\mu^2-1)^2(\mu^2+2)^2}{\mathrm{N}\lambda^4}$$

per unit volume, which is distributed over a solid angle 4π. The fraction of the total diffused energy caught by lens L is only $a \Big/ \frac{16\pi r^2}{3}$ of the whole, where a is the area of the lens. In the case of the incident light the fraction of energy caught by the lens is $a/4\pi r^2 \sin^2 \frac{\theta}{2}$, where θ is the angle of convergence of light. Taking this correction into account the ratio was calculated. From this, and putting $R = 1{\cdot}37 \times 10^{-16}$ per molecule; 42×10^{-12} dynes/cm.^{2}; $T = 305°$; $\mu = 1{\cdot}337$, N was evaluated (taking into account the Cabannes factor) and found to be $7{\cdot}3 \times 10^{23}$, which is of the right order of magnitude.

Summary.

The paper deals with the problem of molecular scattering and extinction of light in liquids, both from the experimental and the theoretical standpoints, and the following are the general results obtained:—

(1) It is shown that the intensity of the light diffused in liquids is not given by the Rayleigh law of scattering. The "Theory of Fluctuations" of density considered by Einstein and Smoluchowski, however, gives a quantitative explanation of the observed phenomena, provided account is taken of the influence of molecular anisotropy which, in general, is very important in the case of liquids.

(2) The light scattered transversely by liquids is, in general, very imperfectly polarized, in fact, far more so than in the case of the vapour of the same substance. It is shown that this fact receives explanation when we consider the general character of the distribution in the liquids of the molecules separately as regards *position* and *orientation*. The theory may be given a quantitative form, and enables the polarization in the liquid to be calculated when that of the vapour is known. Good agreement with facts is observed in the case of some liquids, but in others it is only qualitatively correct.

(3) In accordance with the indications of theory, the intensity of scattering increases with the temperature in liquids and becomes very large as the critical point is approached. The polarization of the scattered light tends at the same time to become more and more perfect.

(4) The state of polarization of the scattered light is found experimentally in liquids to be a function of the wavelength of the incident light, and this indicates that the observed optical anisotropy is probably connected with the

resonance frequencies of the molecules in different directions and with the dispersive properties of the substance.

(5) The absolute determination of the light scattering in liquids enables the Avogadro constant to be evaluated.

Further work with the subject is in progress.

Calcutta,
1st of June, 1922.

Note added in proof dated 11th Dec. 1922.—A fuller discussion of the effect of molecular anisotropy on the scattering and extinction of light in liquids, based on the electron theory of dispersion, will appear in a paper by Mr. K. R. Ramanathan shortly to be published. In his treatment, the fact that the electric polarization is not the same within the liquid as outside it is considered and taken into account.

LXIV. *Intelligence and Miscellaneous Articles.*

ON THE VISCOSITY OF GASES IN A TRANSVERSE ELECTRIC FIELD.

To the Editors of the Philosophical Magazine.

GENTLEMEN,—

IN a paper published in your June number of 1922 on "Viscosity of Air in a Transverse Electric Field," Mr. Satyendra Ray communicates experiments to test whether there is a change in the viscosity of air in a transverse electric field. In *Zeitschrift f. Physik*, I am publishing now a paper which treats this subject from the point of view of the kinetic theory of gases, assuming that the molecules are electric quadruples acquiring in an electric field a momentum proportional to the field-strength. In a field of 100 C.G.S. units the ratio of the viscosity in a transverse field to the viscosity without field would be

$$\text{for nitrogen} = 1 - 4 \cdot 10^{-9},$$
$$\text{for oxygen} = 1 - 3 \cdot 10^{-9}.$$

Mr. Ray found the absence of change in the viscosity of air greater than or equal to 0·3 per cent. in a transverse field of in 60 C.G.S. units, which is in accord with my calculations.

Institut f. theoretische Physik
an der Universität, Vienna.
Dec. 7, 1922.

Yours faithfully,
H. SIRK.